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Composition of Low-Temperature Thermal Extracts  
Obtained from Colorado Oil-Shale Kerogen

W. E. Robinson and J. J. Cummins

Laramie Petroleum Research Center  
Bureau of Mines, U. S. Department of the Interior  
Laramie, Wyoming

The oil shale used in this study is a sedimentary rock containing various amounts of organic material (commonly called kerogen), which was derived from decomposition of aquatic organisms. Associated with the kerogen are large quantities of calcite and dolomite, with smaller amounts of clay minerals, quartz, pyrite, etc. The kerogen is a light-brown mixture of solids having no appearance of oil and is only partly soluble in organic solvents at room temperature. At present, it has not been possible to separate the organic and inorganic phases completely, consequently, most kerogen constitutional studies have been conducted on degradation products.

One method of degradation consists of heating kerogen at various temperatures to obtain soluble products. When retorted at about 500° C. (932° F.), kerogen can be converted to crude shale oil, gases and carbon residue. As approximately 35 percent of the kerogen is cracked to gases and carbon residue by retorting, this method of degradation is not suitable for constitution studies. Kerogen can also be converted to soluble products at temperatures from 200° to 350° C. (392° to 662° F.), however, at a much slower rate. Extensive cracking of kerogen does not occur at these temperatures; consequently, the soluble products obtained by this thermal degradation should contain many of the structures present in the original kerogen.

Samples of raw oil shale were extracted with tetralin at 25° to 350° C. for 24 to 144 hours. As a result, kerogen was degraded to a soluble material, with production of no or very little pyrolytic gases at 300° C., and only about 6% of the kerogen was degraded to gases at 350° C. There was no evidence of the formation of carbon residue at any temperature. The crude extracts were fractionated into oils, waxes, resins, and pentane-insoluble material and characterized by ultimate analyses, ring analyses, x-ray diffraction, mass and infrared spectra, and chemical treatment.

This study showed that the composition of the extracts depended upon the time and temperature of extraction. At constant time of extraction, the pentane-insoluble material increased with increase in temperature of extraction, while the percentage of resins decreased with increase in temperature over the range studied. The percentage of oil remained nearly the same, while the wax content increased slightly at the higher temperatures. The composition of the extracts indicated that kerogen is composed predominantly of saturated heterocyclic structures and smaller amounts of straight-chain paraffins, cyclic paraffins, and aromatic structures. These conclusions agree with and supplement those reported earlier (6,7) from oxidation studies.

Information concerning the constitution of the kerogen present in oil shale, the processes by which it is degraded to useful products, and the composition of its degradation products is needed for developing new and more economical methods of processing this natural resource. It was the purpose of this study to obtain information concerning the nature of kerogen and the low-temperature pyrolytic products obtained from it.

# EXPERIMENTAL PROCEDURE

Materials. Alumina XF21 grade, 80-200 mesh (Alumina Company of America), preheated at 700° C. (1292° F.) for two hours before use.

Silica gel, analytical grade, 28-200 mesh (Davidson).

Tetralin, C<sub>10</sub>H<sub>12</sub>, B. p. (205° - 208° C.), Matheson, Coleman, and Bell, contained 0.04% residue after steam distillation. When heated to 350° C. for 48 hours in absence of air, the purified tetralin contained an additional 0.05% residue after steam distillation.

Apparatus. Reaction vessel, 2000-ml. pressure apparatus (Parr Instrument Company Series 4500) equipped with stirring mechanism to stir contents one minute of each 30 minutes of extraction.

Chromatographic columns, glass columns having three sections (lower section 1.0 cm. x 85 cm., middle section 1.5 cm. x 42 cm., and top section 3.5 cm. x 22 cm.), water-jacketed, and fitted with adapter so 10 to 15 p.s.i.g. nitrogen pressure could be applied to the column.

Oil-Shale Sample. The oil shale was obtained from the Mahogany zone of the Green River formation at the Bureau of Mines Experimental Mine near Rifle, Colo. The sample contained approximately 35% organic material (28.5% organic carbon) and assayed 66 gallons of oil per ton of shale by the modified-Fischer-retort method (8). For use in this study the oil shale was crushed and screened to pass a sieve of 100 meshes per inch.

Preparation of Extracts. Successive batches of 350 grams of oil shale were placed in the reaction vessel with 610 ml. of tetralin (2.3 ml. tetralin per gram of shale), and each batch was extracted 48 hours at 25° to 350° C. (Two series of extractions were made using tetralin as solvent for 48 to 144 hours at 200° C. and 24, 48, 96, and 144 hours at 350° C.) After cooling to room temperature, the vessel was opened and the contents removed. The shale residue was centrifuged from the extract and solvent, then extracted with benzene until free of tetralin and soluble material. The shale residue was air-dried and retained for analysis. The tetralin and benzene extracts were combined and then steam-distilled to remove the solvents. After removal of the tetralin, the extract was recovered from the water phase by solution in benzene. Most of the water was removed from the benzene solution of the soluble extract by means of a separatory funnel and the last trace by azeotropic distillation. Benzene was removed from the extract by atmospheric distillation and the final traces by drying at 80° C. under reduced pressure. (All extracts were dried under these conditions.) By treating several batches of oil shale at different temperatures in the presence of tetralin for 48 hours, the following total amounts of extracts were obtained: 77 grams of extract at 25° C., 18 grams at 200° C., 165 grams at 250° C., 165 grams at 300° C., and 106 grams at 350° C.

The percentage of kerogen extracted from the raw shale was determined from comparison of the kerogen-to-ash ratios obtained before and after the oil shale was extracted. Following is an expression of this relationship:

$$\left[ \frac{\text{Kerogen after extraction, \%}}{\text{Ash after extraction, \%}} \div \frac{\text{Kerogen before extraction, \%}}{\text{Ash before extraction, \%}} \right] \times 100 = \text{Unextracted kerogen, \%}$$

The percentage of kerogen was determined from an ash and mineral CO<sub>2</sub> analyses and equaled 100 minus the sum of the ash and mineral CO<sub>2</sub>. This method of computing the percentage of kerogen decomposed was based upon the assumption that the mineral portion of the raw oil shale was unaltered by the thermal solution treatment.

The extractions were made at the pressure generated by the solvent plus pyrolytic gases that formed at the temperature of extraction. Hot pressures ranged from 80 p.s.i.g. at 250° C. to 700 p.s.i.g. at 350° C., while cold pressures ranged from 40 p.s.i.g. for the 250° C. extraction to 200 p.s.i.g. for the 350° C. extraction (pyrolytic gases).

The dried extracts were fractionated by a procedure outlined in figure 1. The purpose of these fractionations was to obtain materials of similar properties for further analyses and study. Because of the complex nature of the material, the method of fractionation employed was not expected to separate individual components.

Fractionation of Extracts Into Oils, Waxes, Resins, and Pentane-Insoluble Material. Ten-gram batches of the crude extracts were dissolved in a 40 : 1 volume ratio of pentane and allowed to stand overnight at 0° C. and then filtered. The pentane-insoluble material was washed with a small quantity of cold pentane (0° C.) and then dried, weighed, and designated as pentane-insoluble material. The soluble material was stripped free of pentane, dried, and weighed. Five-gram batches of the pentane-soluble material were placed on a pretreated column of alumina (25 : 1 weight ratio of alumina to sample) and eluted with pentane followed by benzene-methanol mixtures and acetone. The pentane-eluted material (oil plus wax) was stripped free of pentane, dried, and weighed. The material remaining on the column was removed by benzene-methanol mixtures and acetone. This material, referred to as resins, was stripped free of solvent, dried, and weighed. Five-gram batches of the oil and wax fraction were dissolved in a 40 : 1 volume ratio of methyl ethyl ketone (MEK) to extract and allowed to stand at -5° C. for 1 hour. The wax was filtered from the MEK-soluble material, dried, and weighed. The MEK was removed from the oil by distillation and the latter was dried and weighed.

Fractionation of Waxes. Urea adducts were prepared by reacting each gram of wax with 21 ml. of a saturated solution of urea in methanol. Excess urea amounting to 1.5 grams per gram of wax plus 6 or 7 drops of benzene was added. This mixture was stirred at room temperature for 14 to 24 hours. The adduct and non-adduct waxes were separated by filtration; the final traces of non-adduct material were removed by washing with 100 ml. each of pentane and isooctane. The adduct was then decomposed with hot water and, after cooling, extracted from the water phase by ether. The adduct wax was freed from ether, dried, and weighed. The pentane-isooctane-methanol solution of the non-adduct was freed from urea by washing with water. The non-adduct wax was freed of solvent by distillation, dried, and weighed.

Fractionation of Oils. The oil was fractionated by a method similar to that reported by Mair et al. (3). Four-gram batches of the oil fraction were placed on a pretreated column of silica gel (25 : 1 weight ratio of silica gel to sample) and eluted successively with isooctane, benzene, and 2-propanol. The three fractions were freed of solvent, dried, and weighed. The isooctane-eluted material was called paraffin oil, the benzene-eluted material was called aromatic oil, and the 2-propanol-eluted material was called polar oil. The paraffin oil was further fractionated into paraffin-oil adduct and paraffin-oil non-adduct by the technique used for waxes. Additional fractionation of the aromatic oil was obtained on a pretreated column of alumina (25 : 1 weight ratio of alumina to sample) by using iso-octenes, benzene, and 2-propanol as eluting solvents. The solvent was removed from each of the fractions, and the oil was dried and weighed.

Physical Properties. The ultimate composition of the crude extracts and the various fractions was determined by conventional methods of analysis: Carbon and hydrogen were determined by a combustion train, nitrogen by Kjeldahl digestion, sulfur by ignition in a Parr oxygen bomb, and oxygen by difference. Densities were determined using pycnometers at 20° or at 40° C. and converting to d<sub>4</sub><sup>20</sup>. Refractive indices were determined using the sodium D line (589 Å) and the mercury g line (436 Å) and were used to calculate specific dispersion for the aromatic fractions. Molecular weights were determined by the rise-in-boiling-point method using benzene

as the solvent. Infrared, ultraviolet, and mass spectra, as well as x-ray diffraction, were used to characterize the various fractions.

**Chemical Properties.** The fractions were oxidized by a method described by Robinson et al. (7) with an excess of alkaline potassium permanganate at the boiling temperature of the solution for 100 hours. Concentrated hydriodic acid (70%) was used to reduce the resin and pentane-insoluble fractions by a method described by Raudsepp (5) in which the fraction plus HI was sealed in a glass tube and heated 24 hours at 200° C. Basic nitrogen was determined for the resin and pentane-insoluble fractions by a method described by Deal et al. (1), in which total basic nitrogen was determined by titration with perchloric acid. Neutral nitrogen compounds were determined as the difference between the basic nitrogen and the total nitrogen.

#### EXPERIMENTAL RESULTS AND DISCUSSION

**Rate of Product Formation.** The amount of conversion of kerogen to degradation products by thermal solution in tetralin was dependent upon the temperature and time of extraction. For constant periods of extraction of 48 hours, the conversion of kerogen to degradation products ranged from 4.4% at 25° C. to 84.9% at 350° C. (table 1). By maintaining the temperature constant at 200° C. and varying the time of extraction, the yield of products ranged from 8.8% for 48 hours to 9.3% for 144 hours of extraction. A comparable series of extractions at a constant temperature of 350° C. showed an increase in product yield of 75.8% for 24 hours of extraction to 94.5% for 144 hours of extraction. This showed that most of the product was obtained during the first part of the extraction, as 80% of the total (for 144 hours) was obtained after 24 hours. An additional 10% was formed in a subsequent 24-hour period with the final 10% requiring 96 more hours of extraction. This suggests that at lower temperatures, where low yields of product were obtained, it would be impossible in finite time to obtain 100% conversion of kerogen to soluble products. Landau and Asbury (2) showed that a straight-line relationship existed between time of extraction and time of extraction divided by percentage yield of extract and that the slope of the line showed the ultimate yield of extract which could be obtained from coal. The calculated ultimate yield from a similar plot of data obtained from oil shale in this study was 9.6% at 200° C. and 100% at 350° C.

TABLE 1. - Tetralin extraction of kerogen from raw shale

Time of extraction, hours	Temperature of extraction, °C.	Kerogen extracted, %
48	25	4.4
48	200	8.8
144	200	9.3
48	250	10.2
48	300	28.7
24	350	75.8
48	350	84.9
96	350	87.9
144	350	94.5

The influence of temperature on the conversion of kerogen to soluble material is shown in figure 2. A gradual increase in yield of product per degree rise in temperature was obtained from 25° to 250° C., while from 300° to 350° C. a rapid increase in yield per degree rise in temperature was obtained. The break in the curve suggested that a change in the thermal solution process took place at approximately 275° C.

Thompson and Prien (9) reported a similar relationship at 300° C. and suggested that the reaction taking place below 300° C. was the desorption of macromolecules of kerogen in which bond energies comparable to van der Waals forces were ruptured. Above 300° C. other secondary bonds were broken. Similar reasoning would indicate that the composition of the products obtained below 300° C. should differ from those obtained above 300° C. Likewise, the molecular weights of the crude extracts obtained at the two temperature ranges probably would be different. Data presented later in this paper only partly confirm these findings.

Ultimate Composition of Crude Extracts. The sulfur and oxygen contents (table 2) of the extracts decreased with increase in temperature and time of extraction. This showed that structures which contained these elements were readily susceptible to thermal degradation. By contrast, the nitrogen structures in kerogen were difficult to degrade and only a small amount of the kerogen nitrogen was evolved in the form of gases. In tests (fig. 3) where the time of extraction was constant at 48 hours and temperature increased, loss of oxygen (probably decarboxylation and dehydration) from the extracts occurred between 200° and 250° C. and continued to 350° C., where only a small portion of the kerogen oxygen remained in the extract. Sulfur contents remained high until a temperature of 350° C. was reached, when loss of sulfur (probably as H<sub>2</sub>S) became rapid. Hydrogen contents remained almost equal to that of the original kerogen over the temperature range. However, nitrogen contents of the extracts increased very rapidly at 300° C. with increase in temperature of extraction and nearly equaled that of kerogen in the 350° C. extract. In the tests where temperature remained constant at 350° C. and the time of extraction varied, similar trends for oxygen and sulfur were obtained (Fig. 4). Overall oxygen and sulfur contents decreased with time of extraction, nitrogen contents remained nearly constant, and the hydrogen contents decreased after 48 hours of extraction. No significant differences were found in the molecular weights of the crude extracts which were prepared at 350° C. and 48 hours of extraction time. However, molecular weights of the extracts decreased with increase in time of extraction at constant temperature of 350° C.

TABLE 2. - Ultimate composition and molecular weight of crude tetralin extracts

Temperature of extraction, °C.	Time of extraction, hours	Atomic ratios x 10 <sup>2</sup>									Molecular weight
		C	H	O <sup>1/</sup>	N	S	H/C	O/C	N/C	S/C	
25	48	80.4	11.1	6.5	0.9	1.1	159	5.8	0.9	0.5	580
200	48	80.8	10.7	6.6	0.9	1.0	159	6.1	0.9	0.5	595
250	48	82.2	10.9	4.9	1.0	1.0	159	4.5	1.0	0.5	555
300	48	82.4	10.5	4.2	1.6	1.3	153	3.8	1.7	0.6	580
350	24	82.7	10.3	3.5	2.4	0.6	157	3.2	2.5	0.3	625
350	48	84.1	11.3	1.0	2.6	1.0	161	0.9	2.7	0.4	535
350	96	85.1	11.0	1.0	2.6	0.3	155	0.9	2.6	0.1	405
350	144	84.7	10.6	1.7	2.6	0.4	150	1.5	2.6	0.2	410

<sup>1/</sup> Oxygen was determined by difference.

Pyrolytic Gases. Approximately 60% of the pyrolytic gas was hydrogen, some of which may have resulted from the dehydrogenation of the tetralin used as solvent. At 350° C. approximately 28% of the oxygen and 19% of the sulfur present in kerogen was removed as pyrolytic gases (table 3) compared to about 3% of the total carbon. This suggested that at this temperature oxygenated groups such as carboxyl or others were degraded to CO<sub>2</sub> and CO, while sulfur groups such as sulfides or others were degraded to H<sub>2</sub>S. By contrast, only a small portion of the kerogen was degraded to

gases at 25° to 300° C. Based on the total kerogen, approximately 6% of the kerogen was degraded to gases at 350° C., 0.2% at 300° C.; and 0.09% at 250° C. This shows that very little of the kerogen was cracked to final degradation products at 300° C. and below, only a small amount of kerogen being converted to gas at 350° C. Also, there was no evidence of the formation of carbon residue at any temperature. Consequently, extracts prepared at these temperatures should contain many of the structures present in the original kerogen.

TABLE 3. - Gases produced by degradation of one kilogram of kerogen

	Gas produced, moles		
	Degradation temperature, °C.		
	250	300	350
Methane	0.003	0.005	0.578
Ethane	-	-	0.163
Propane	0.004	0.008	0.078
n-Butane plus isobutane	-	-	0.020
n-Pentane plus isopentane	-	-	0.007
Carbon dioxide	0.007	0.013	0.637
Carbon monoxide	0.011	0.021	0.013
Hydrogen	0.040	0.081	2.677
Hydrogen sulfide	-	-	0.065
Nitrogen	-	-	0.208
Total gas produced	0.065	0.128	4.446

Product Distribution. The percentage of pentane-insoluble material present in the extracts increased with increase in temperature of extraction at 250° to 350° C. (fig. 5), while the wax content of the extracts increased at 300° and 350° C., where time of extraction was constant at 48 hours. By contrast, resin contents decreased continuously with increase in temperature over the temperature range. Oil content increased at 200° C. and decreased slightly at 350° C. This showed that the composition of the extracts was dependent upon the temperature of extraction. Ultimate compositions and molecular weights of these fractions are shown in table 4.

In the series of tests at 350° C., where time of extraction was varied from 24 to 144 hours, pentane-insoluble material decreased from 48 to 21% with increase in time of extraction. On the other hand, resins increased from 18 to 29%, oils from 27 to 37%, and wax from 7 to 13%. This showed that approximately half of the pentane-insoluble material was degraded into oil, wax, and resins at 350° C. after 144 hours of extraction.

Constitution of Waxes. The constitution of the wax fractions produced at the temperatures studied showed limited variation. The percentage of adduct (predominantly straight chain structures) obtained from the wax tended to decrease with increase in temperature of extraction as the 25° C. wax produced 72% wax adduct compared to 51% for the 350° C. wax (see table 5). Also, the non-adduct wax was predominantly naphthenic. Mass spectra showed that the straight-chain portion of the waxes tended to decrease in carbon chain length as the temperature of extraction increase, for example: The average chain length was 30 for the 25° C. wax adduct, 28 for 250° C. wax adduct, and 25 for 350° C. wax adduct. X-ray diffraction showed that the non-adduct wax fractions had an average chain length less than 16 carbon atoms. The wax adduct fractions contained an average of 2.0 to 2.4 methyl groups per molecule, which indicated little or no branching. The cyclic portion of the wax contained 1 to 6 rings with 3 to 4 rings predominating. The

TABLE 4. - Ultimate composition and molecular weights of the major fractions

	C	H	Cl/	N	S	Atomic ratios x 10 <sup>2</sup>			Molecular weight	
						H/C	O/C	N/C		
						S/C				
25° C. Extract										
Pentane-insoluble material	80.1	11.3	7.4	0.2	1.0	169	6.9	0.2	0.5	1320
Resin	78.9	11.0	7.8	0.9	1.4	167	7.4	1.0	0.7	625
Wax	83.6	13.8	2.3	0.2	0.1	198	2.1	0.2	0.04	415
Oil	86.7	12.2	0.7	0.1	0.3	169	0.6	0.1	0.1	350
200° C. Extract										
Pentane-insoluble material	78.3	10.5	8.6	1.7	0.9	161	8.2	1.9	0.4	1250
Resin	80.3	10.8	6.5	1.1	1.3	162	6.1	1.2	0.6	605
Wax	84.8	13.8	0.8	0.2	0.4	195	0.7	0.2	0.2	480
Oil	86.5	12.4	0.5	0.1	0.5	172	0.4	0.1	0.2	350
250° C. Extract										
Pentane-insoluble material	81.4	10.6	4.8	2.2	1.0	156	4.4	2.3	0.5	1290
Resin	79.9	10.4	7.0	1.5	1.2	156	6.6	1.6	0.6	570
Wax	84.6	14.3	0.9	0.1	0.1	203	0.8	0.1	0.04	440
Oil	87.2	11.7	0.7	0.1	0.3	161	0.6	0.1	0.1	365
300° C. Extract										
Pentane-insoluble material	81.4	10.3	4.0	3.0	1.3	152	3.7	3.2	0.6	1210
Resin	78.3	10.4	8.6	1.8	0.9	159	8.2	2.0	0.4	650
Wax	84.8	13.9	1.0	0.1	0.2	197	0.9	0.1	0.09	415
Oil	87.5	11.7	0.2	0.1	0.5	160	0.2	0.1	0.2	340
350° C. Extract										
Pentane-insoluble material	81.2	9.9	4.1	3.8	1.0	146	3.8	4.0	0.5	1280
Resin	83.3	10.9	2.4	2.9	0.5	157	2.2	3.0	0.2	575
Wax	86.1	13.3	0.2	0.2	0.2	185	0.2	0.2	0.09	355
Oil	86.8	12.2	0.3	0.4	0.3	169	0.3	0.4	0.1	375
/ Determined by difference.										

1/ Determined by difference.

average molecular weight of the crude-wax fraction (before fractionation by the formation of urea adducts) ranged from 355 to 480 and tended to decrease with increase in temperature of extraction from 25° to 350° C. Ultimate composition of the unfractionated wax showed minor variations and averaged 84.8% carbon, 13.8% hydrogen, 1.0% oxygen (by difference), 0.2% nitrogen, and 0.2% sulfur.

TABLE 5. - Carbon distribution of wax fractions

Temperature of extraction, °C.	Carbon-type composition		Percentage of total wax
	% C <sub>N</sub>	% C <sub>P</sub>	
Wax (adduct) 1/			
25	9	91	71.5
250	12	88	55.6
350	12	88	50.5
Wax (non-adduct) 1/			
25	78	22	28.4
250	66	34	44.4
350	78	22	49.5

1/ Determined from mass spectra.

**Constitution of Oils.** The composition of the oil fractions tended to become more aromatic and less paraffinic with increase in temperature of extraction (see fig. 6). In general, the percentage of paraffin oil non-adduct decreased with increase in temperature of extraction, the aromatic and polar oil fractions increased with increase in temperature, while the paraffin oil adduct remained nearly the same. Utilizing physical property data, ring analyses were determined for the paraffin oil non-adduct fraction by the n-d-M method (10) and for the aromatic oil by the Martin method (4). Mass spectra were used to determine the amount of straight-chain and cyclic paraffins present in the paraffin oil adduct. The results of these analyses are shown in table 6. Based on these data approximately 33% of the 25° C. oil consisted of straight-chain paraffins, 48% cyclic paraffins, 16% aromatics, and 3% polar oil. The 350° C. oil was more aromatic as it contained 18% straight-chain paraffins, 26% cyclic paraffins, 36% aromatics, and 20% polar oil.

TABLE 6. - Ring analysis and molecular weight of oil fractions

Temperature of extraction, °C.	Carbon-type composition			Molecular weight
	% C <sub>A</sub>	% C <sub>N</sub>	% C <sub>P</sub>	
	Paraffin oil (adduct) 1/			
25	0	72	28	405
250	0	80	20	380
350	0	82	18	285
	Paraffin oil (non-adduct) 2/			
25	6	57	37	430
250	0	75	25	415
300	1	58	41	345
350	3	47	50	370
	Aromatic oil (0-2-1) 3/			
25	45	25	30	300
250	46	37	17	290
350	81	12	7	305

1/ Determined from mass spectra.

2/ Determined by n-d-M method.

3/ Determined by Martin method.

The percentage of aromatic compounds in the 350° C. oil may be too high because of extraneous materials that were obtained from the tetralin used as solvent. Based upon the amount of extract produced and the amount of tetralin residue obtained at 350° C., approximately 0.7% of the total extract may have been derived from the tetralin. Because of small yields, as much as 5% of the total 25° C. extract may have come from this source. The composition of the 350° C. oil was corrected for an assumed amount of 5% (based on total oil) of aromatic oil which may have been derived from the solvent. After this correction the 350° C. oil contained approximately 19% straight-chain paraffins, 27% cyclic paraffins, 33% aromatics, and 21% polar oil.

The paraffin-oil adduct fraction had an average of 2.6 to 3.4 rings per molecule, the paraffin-oil non-adduct had 2.8 to 5.1 rings per molecule, and the aromatic oil eluted with isooctenes had an average of 3.0 to 4.0 rings per molecule. (The latter fraction represented 95% of the aromatic oil.) The aromatic-oil fraction (isooctene eluted) had an average of 22 carbon atoms per molecule and a determined molecular weight of 305. Mass spectra of this fraction showed that every homologous series was present in percentages ranging from 10 to 19%.

The molecular weights of the oil fraction before fractionation ranged from 340 to 375 and showed no correlation to temperature of extraction. Likewise, the elemental composition of the oil fractions showed very little variation and averaged 86.9% carbon, 12.0% hydrogen, 0.5% oxygen, 0.2% nitrogen, and 0.4% sulfur.

**Constitution of Resins.** Significant differences in the elemental composition of the resin fractions were found (fig. 7). In general, oxygen, hydrogen, and sulfur contents of the resin fractions decrease with increase in temperature of extraction. The oxygen content of the resins decreased at temperatures from 25° to 200° C., reached a maximum at 300° C., and decreased very rapidly at 350° C. This showed that rapid degradation of oxygenated structures occurred between 300° and 350° C., probably resulting in the formation of CO and CO<sub>2</sub>. Hydrogen-to-carbon ratios gradually decreased over the temperature range indicating the presence of an easily dehydrogenated material, while sulfur contents tended to decrease only at the higher temperatures. By contrast, nitrogen-to-carbon ratios increased with increase in temperature over the temperature range. These results suggested the following: (1) Oxygen structures present in resins are readily made soluble and are easily degraded further to CO<sub>2</sub>, CO, and perhaps water. (2) Nitrogen structures present in resins are difficult to make soluble and are quite stable to further degradation. From bond energies it appears that kerogen contains more C=N structures, which have higher bonding energies, than C-N structures. (3) Loss of hydrogen from the resins at all temperatures indicated that easily dehydrogenated structures such as partly unsaturated cyclic structures, isoprenoid, steroid, or similar structures are present in kerogen. (4) Loss of sulfur at 300° and 350° C. indicated the presence of some unstable sulfur compounds.

The molecular weights of the resin fractions ranged from 570 to 650 and did not appear to be related to the temperature of extraction.

The resin fraction obtained from the 350° C. extract was subjected to oxidation by an aqueous solution of alkaline potassium permanganate and approximately 75% of the resin was unoxidized. Comparable tests on the oil fraction from this extract showed that 71% of the oil remained unoxidized, also, comparable ratios of K<sub>2</sub>MnO<sub>4</sub> to carbon were consumed in both tests. This shows that approximately the same amount of structures, which are resistant to oxidation, are present in the resins as are present in the oils. The resin contained 3.0% nitrogen, however, this did not alter the oxidation appreciably from that of the oil which contained only 0.4% nitrogen. This suggested the presence of cyclic nitrogen structures which may be stable to K<sub>2</sub>MnO<sub>4</sub> oxidation.

The 350° C. resin fraction was subjected to reduction by hydriodic acid; approximately 38% of the resin was reduced to oil, 2% to wax, and 60% remained unchanged. This indicated that approximately 40% of the resin had structures similar to that present in the oil and wax fractions.

Infrared spectra of the resin fractions indicated the presence of hydroxyl and carbonyl groups and that the amount of hydroxyl groups tended to increase with increase in temperature of extraction. The band indicating the presence of four or more methylene groups appeared to be weak which showed the presence of only small amounts of large side chains. Carboxyl groups, in addition to hydroxyl groups, appeared to be present in the extracts prepared at higher temperatures.

Basic nitrogen determinations on the resin fractions showed that the ratio of basic nitrogen to total nitrogen ranged from 0.44 for the 25° C. resins to 0.34 for the 350° C. resins. Thus, the neutral nitrogen present in the resins tended to increase with increase in temperature of extraction and represented from 56 to 66% of the total nitrogen.

Constitution of Pentane-Insoluble Material. The composition of the pentane-insoluble fractions (fig. 8) showed trends similar to those of the resin fractions. In general, oxygen, hydrogen, and sulfur contents decreased with increase in temperature of extraction, while nitrogen contents increased with temperature of extraction. The same general conclusions concerning hetero structures can be made for the pentane-insoluble material as were made for the resin fractions in the preceding section. There was, however, one difference in that the loss of oxygen from the pentane-insoluble material occurred between 200° to 350° C. compared to 300° to 350° C. for the resin fraction. This suggested differences in the type of oxygenated structures present in the two materials. Also, the pentane-insoluble material produced at higher temperatures appeared to contain less hydrogen and more nitrogen than the resins. The molecular weights of the pentane-insoluble material ranged from 1210 to 1320 and showed no relationship to temperature of extraction.

Oxidation of the 350° C. pentane-insoluble material in a manner similar to that used for resins showed that 25% of this fraction was resistant to oxidation compared to 70 to 90% for resins, oils, and waxes and only 5% for kerogen. This showed that the pentane-insoluble fraction contained less structures which were resistant to oxidation than the oil, wax, or resin fractions. About 40% of the pentane-insoluble material was oxidized to non-volatile non-oxalic acid compared to 1% for kerogen, 9% for resins, 17% for oil, and 0% for waxes. This suggested the presence of benzenoid acids that may have been derived from benzenoid structures present in the pentane-insoluble material. These structures probably were not in the kerogen as such but were formed during the thermal solution by dehydrogenation of partly unsaturated cyclic structures present in kerogen.

A comparable reduction test to that used for the resin fraction was made on the pentane-insoluble material. Approximately 25% of the material was reduced to oil, wax, and resins and 75% remained unchanged. These data showed that the pentane-insoluble material contained approximately 25% structures similar to oils, waxes, and resins.

Infrared spectra of the pentane-insoluble fraction indicated the presence of hydroxyl, carboxyl, and aromatic groups. The structure appeared to be predominantly cyclic but may contain considerable chain branching and substitution at the higher temperatures of extraction.

Basic nitrogen determinations on the pentane-insoluble fractions showed that the ratio of basic nitrogen to total nitrogen ranged from 0.29 to 0.36 and was not related to the temperature of extraction. Therefore, the amount of neutral nitrogen

ranged from 64 to 71% of the total nitrogen and was slightly higher than that present in the resin fractions.

#### SUMMARY AND CONCLUSIONS

Based upon the weight-percent of total extract obtained at constant periods of extraction time, the amount of wax and pentane-insoluble material increased with increase in temperature of extraction, the percentage of resins decreased with increase in temperature, and the percentage of oil remained nearly the same. At constant temperature of extraction (350° C.), the percentage of pentane-insoluble material decreased with increase in time of extraction and the percentage of oil, wax, and resins increased with increase in the period of extraction.

The elemental composition of the oil and wax produced over the temperature range remained nearly the same. By contrast, the composition of the resin and pentane-insoluble fractions depended upon temperature of extraction; however, no correlation was established between the composition of extracts and the increased rate of conversion to degradation products obtained at about 275° C. Oxygen content of the resin and pentane-insoluble fractions decreased with increase in temperature of extraction and indicated that oxygen structures present in kerogen are readily degraded. Nitrogen content of the resin and pentane-insoluble fractions increased with increase in temperature of extraction and indicated that nitrogen structures present in kerogen are quite stable and are not readily made soluble. Although differences were found in the composition of the extract fractions, the average molecular weights of the oil, wax, resin, and pentane-insoluble fractions did not change appreciably with increase in temperature of extraction.

At 350° C. kerogen was degraded to approximately 10 to 15% straight-chain paraffins containing 25 to 30 carbon atoms, 20 to 25% naphthenic and 10 to 15% aromatic structures having an average of 3 to 5 rings per molecule, and 45 to 60% heterocyclic material. These materials are probably representative of structures present in the original kerogen and suggest that kerogen is predominantly a heterocyclic material connected to or associated with smaller amounts of hydrocarbon material consisting of straight-chain, cyclic paraffin, and aromatic groups.

#### ACKNOWLEDGMENT

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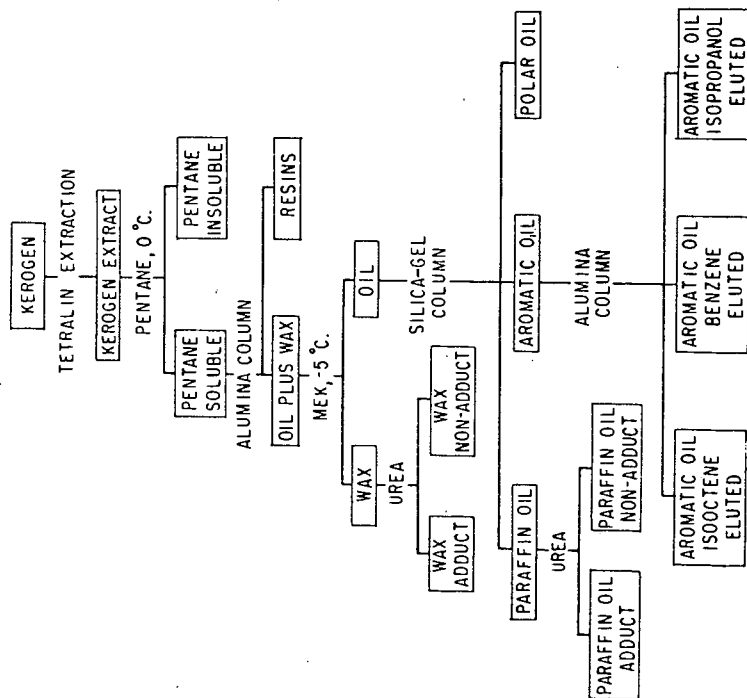


FIGURE 1.-FLOW DIAGRAM OF FRACTIONATION PROCEDURE.

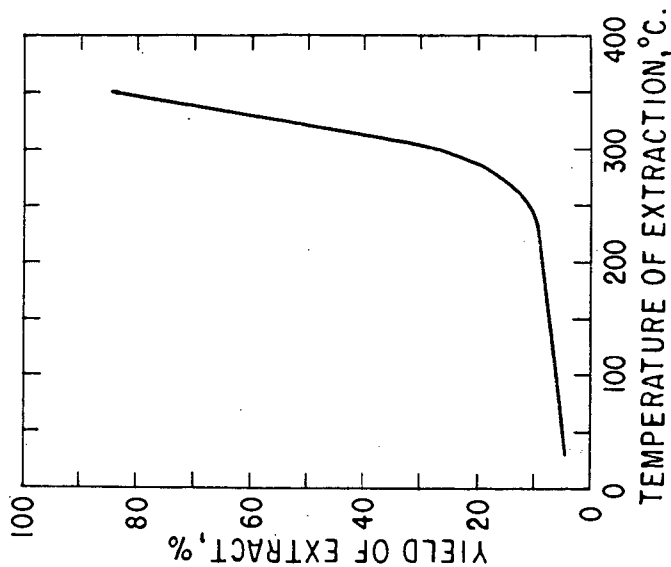


FIGURE 2.-INFLUENCE OF TEMPERATURE ON EXTRACTION OF KEROGEN FOR 48 HOURS.

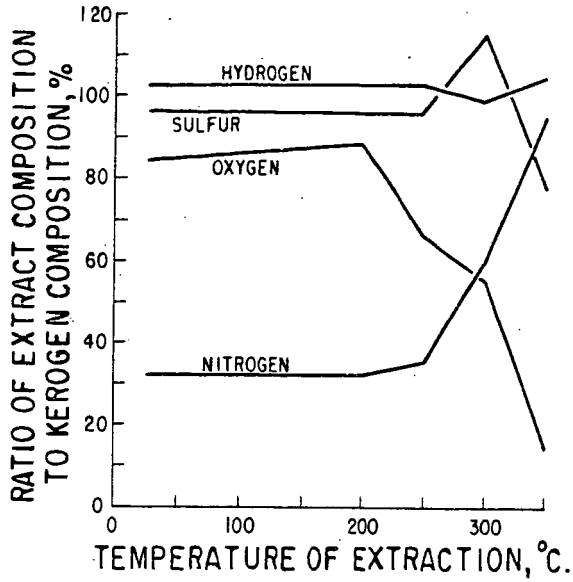


FIGURE 3.-RELATIONSHIP OF EXTRACT COMPOSITION TO TEMPERATURE OF EXTRACTION FOR CONSTANT PERIOD OF TIME.

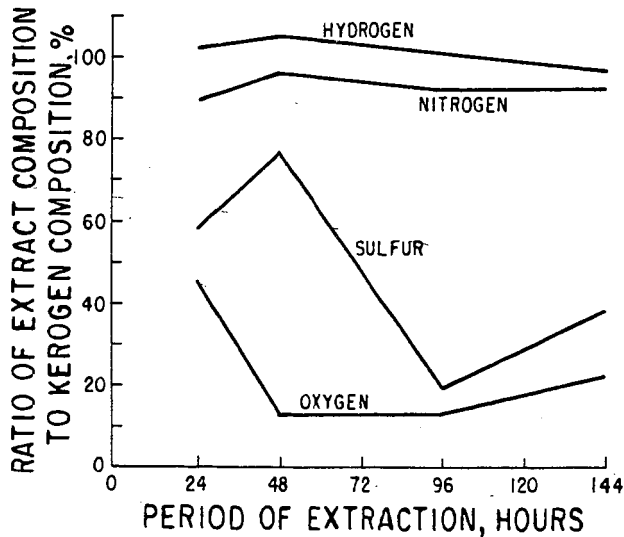


FIGURE 4.-RELATIONSHIP OF EXTRACT COMPOSITION TO PERIOD OF EXTRACTION AT CONSTANT TEMPERATURE.

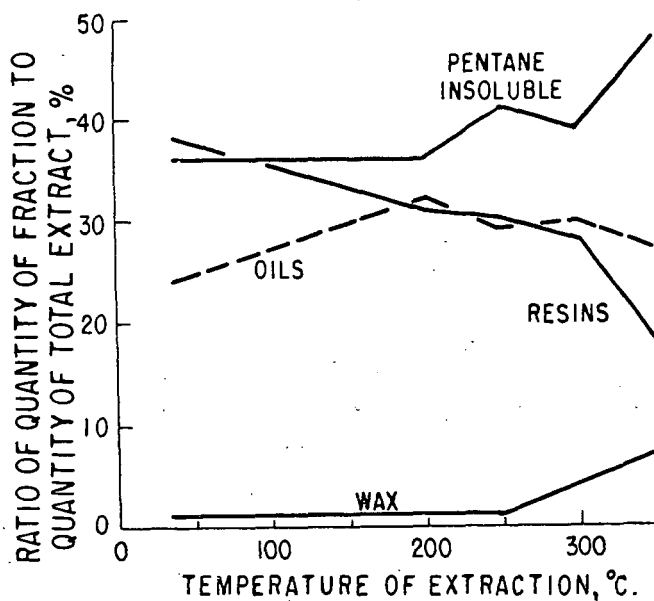


FIGURE 5.-RELATIONSHIP OF FRACTION DISTRIBUTION TO TEMPERATURE OF EXTRACTION.

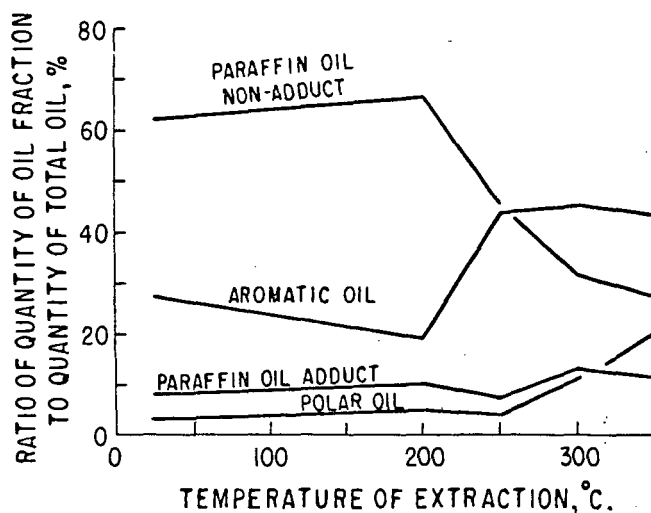


FIGURE 6.-RELATIONSHIP OF THE DISTRIBUTION OF OIL FRACTIONS TO TEMPERATURE OF EXTRACTION.

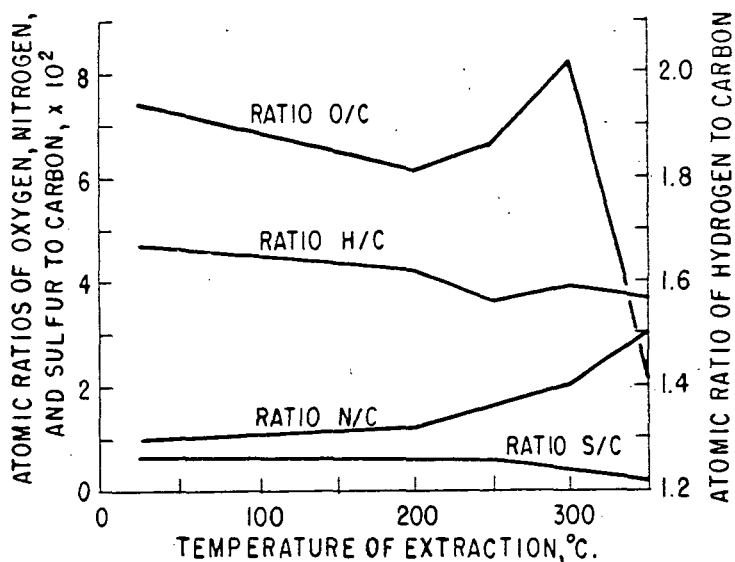


FIGURE 7.-COMPOSITION OF RESIN FRACTION AT VARIOUS TEMPERATURES.

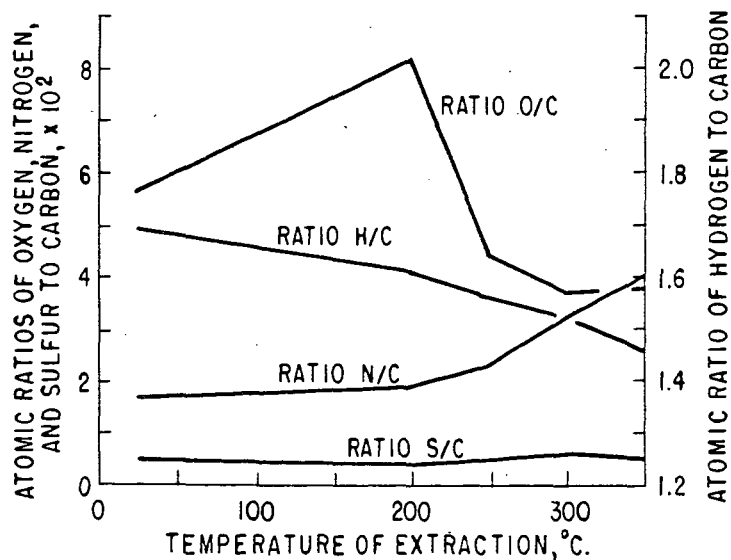


FIGURE 8.-COMPOSITION OF PENTANE-INSOLUBLE FRACTIONS AT VARIOUS TEMPERATURES.

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Solvent Refining of Low Temperature Tar  
With Paraffinic Solvents

M. D. Kulik and M. B. Neuworth

CONSOLIDATION COAL COMPANY  
Research and Development Division  
Liberty, Pennsylvania

Commercial refining of coal tar is based on a primary separation involving either atmospheric or vacuum distillation. The tar is separated into a distillate fraction and a non-volatile pitch fraction. The high molecular weight character and thermal instability of most tars limits the amount of distillate from 50 to 60% of the raw tar. These factors have influenced the utilization of tar to a considerable extent.

Solvent refining of tar is of interest as an alternate primary fractionation method since it might overcome the major limitations of the distillation process. The temperatures required for solvent refining are usually considerably lower than the maximum temperatures reached in distillation and consequently less destructive to the thermally sensitive tar components. In addition, separations based on chemical structure can be effected depending on the choice of solvent.

Low temperature coal tar is composed of an extremely broad and complex mixture of tar acids, nitrogen bases, sulfur compounds, neutral hydrocarbons in various degrees of unsaturation or cyclization and heterocyclic structures. It was therefore of interest to determine what separations were possible by solvent refining.

The results of earlier investigators on solvent refining of coal tars can be divided into two categories depending on the class of solvent used. Extractions carried out by Sinnatt<sup>(1,2)</sup> with polar solvents including methanol, ethanol, pyridine, etc., resulted in essentially complete solubility of the tar. Extraction of tar with paraffinic hydrocarbons, pentane to decane, carried out by Jacobsen<sup>(3)</sup> and Weindel<sup>(4)</sup> resulted in the solution of 40 to 60% of the tar. There have been no studies reported on the refining of raw low temperature coal tar with low boiling paraffinic hydrocarbons under pressure which would permit an evaluation of the important extraction variables.

Kuhn<sup>(5)</sup> examined the propane refining of a pentane extract from high temperature tar. This extract represented 38% of the raw tar. At extraction temperatures of from 30 to 90°C yields of propane extract varied from 5 to 72% of the pentane soluble tar. The yield of extract was essentially independent of temperature varying directly with the solvent ratio. The separation effected by propane appeared to be principally on the basis of molecular weight. In addition, oxygen, nitrogen and sulfur containing compounds concentrated in the propane reject.

In our investigation, a study was made of single-stage batch extraction of low temperature coal tar with paraffinic solvents from propane through hexane. An apparatus was designed in which extraction of tar or tar fractions could be made over a wide range of temperatures and which permitted precise material balances. The effect of solvent molecular weight, solvent structure, solvent ratio and extraction temperature has been correlated with the yield and composition of extract and raffinate tars.

#### EXPERIMENTAL

The extraction apparatus consisted of a 2-liter capacity Parr stirred autoclave modified as shown in Figure 1. The bottom of the bomb was equipped with a 1/4-inch stainless steel valve and drain tube to provide bottom withdrawal of the liquid contents. This permitted the reactor to be used as a pressure separatory funnel. An autoclave skin thermocouple was employed in addition to the inner thermocouple to prevent excessive bomb surface temperature which might polymerize the thermally sensitive tar components. To keep the viscous pitch fluid and mobile, the drain tube was provided with a nichrome heating element. This tube extended into a round bottom flask which served as the product receiver and flash still. A water-cooled condensing system followed by a dry ice trap condensed the flash distilled solvents. Propane, butane and pentane were charged to the reactor from the transfer bomb by nitrogen pressure. Recovery of the more volatile solvents was measured by the wet test gas meter.

The autoclave was charged with 250 to 600 gms of filtered Disco tar which contained 2.0% moisture. The tar volume was calculated as moisture-free with a specific gravity at 25/25°C of 1.100. The amount of solvent to be added was computed, the required amount volumetrically measured, weighed and chilled to -20°C to minimize solvent loss in transfer to the opened autoclave. However, the more volatile solvents, propane, butane and pentane, were charged to the assembled reactor quantitatively by weight difference from the nitrogen pressurized transfer bomb. After the reactor was sealed, the inner bomb temperature was brought to the desired level in approximately one hour and the temperature held constant during agitation for 15 minutes. Separation of the phases by gravity settling was allowed for 1/2 hour. The lower phase (pitch or raffinate phase) was drawn off through the heated drain tube and appeared as a frothy gelatinous mass. The interface was recognized when a sudden burst of gas was emitted from the drain tube due to the flash vaporization of the volatile solvent-rich extract phase. At this time the gelatinous frothy nature of the draining liquid disappeared. For collection of the extract phase, the receiver was replaced by a clean one and the extract tar and flashed solvent collected separately. Further separation of solvent from the product was done by fractional distillation. Propane and butane recovery was measured by a wet test gas meter. Overall material balances ranged from 98 to 100%. All solvents used were 95% or higher in purity except pentane which was a commercial grade of 90% purity.

#### DISCUSSION OF RESULTS

The yield of extract tar is dependent upon three factors, that is, the intrinsic solvent properties, solvent ratio and temperature. If the temperature is maintained constant at 100°C and extract yield is plotted against solvent ratio, extract yield increases with increased solvent boiling point or carbon chain length as shown in Figure 2. Thus at a solvent ratio of 2.5 n-butane yields 42% extract, n-pentane 57% and hexane 70%.

The branched chain solvents behave more like a lower molecular weight straight chain analogue, for example, the yield of extract using isopentane, falls between the yields observed for n-butane and n-pentane. The branched paraffin, 2,3-dimethyl butane, in a similar comparison yields 62% extract, a value between the yields for n-hexane and n-pentane. Thus, if the boiling points of the solvents are plotted against extract yield at a solvent ratio or 2.5, the relationship is very nearly defined by a straight line function.

At a constant temperature of 100°C a solvent ratio greater than 2.5 has very little effect upon yield. This is particularly true of the solvents boiling above n-butane. When the hexane ratio is decreased below 2.5 the yield of extract increases to 78% at 0.75 solvent volumes. Decreasing the solvent ratio further results in slow and uncertain phase separations. It is estimated that complete solubility of the tar, that is, the plait point is attained at a solvent ratio of 0.6. Pentane behaves in a similar manner, however, the plait point is somewhat lower and is estimated at a solvent ratio of 0.5. Lowering the butane or propane solvent ratio below 2.5 results in a reverse effect on yield in contrast to that obtained with pentane and hexane. The yield of extract using butane drops to 37% at a solvent ratio of 1.

The effect of temperature upon the yield of extract tar obtained with hexane and butane is summarized in Figure 3. The higher temperature produces a considerable increase in yield. Thus at a solvent ratio of 2.5 the yield at 100°C of 71% is increased to 78% at 150°C. Butane in comparison exhibits the reverse effect with temperature and gives lower yields at the higher temperature. By raising the temperature from 100°C to 150°C the yield at a solvent ratio of 2.5 decreases from 44 to 43%. At a solvent ratio of 4.5 this decrease in yield with increased temperature is even more pronounced and drops from 51 to 44%. This decrease in yield with butane at the higher temperature may be attributed to the low critical temperature of butane (153°C) for at 150°C butane approaches the completely gaseous state. Hexane exhibits the more normal liquid solvent behavior because at 150°C it is below its critical temperature of 235°C. Pentane shows the same effect of temperature as hexane. Similar results were obtained by Kuhn<sup>(5)</sup> on propane extraction of pentane extract from high temperature tar. Kuhn showed that the yield of extract was directly proportional to the solvent ratio and essentially independent of the temperature.

The efficiency and selectivity of fractionation of the tar by the solvents was measured by the ability of the solvent to produce an extract of low asphaltene content. Asphaltenes were measured as that fraction of the extract tar sample which was insoluble at 25°C in 120 volumes of petroleum ether, which had a boiling range of 30-65°C. The feed tar contained 24.8% asphaltenes. The asphaltene contamination of the tar extract fractions with temperature, solvent, and solvent ratio as parameters was determined and is shown in Figure 4. Increase in extraction temperature shows that a particular solvent became less selective as indicated by the increased asphaltene contamination of the extract. For example, hexane at 150°C shows an extract tar asphaltene contamination of about 23% and only 18% at 100°C. A similar broad change is noticed with pentane and butane. The lower the boiling point of the solvent, the greater selectivity it exhibits at a given temperature and solvent ratio. Thus, at 100°C, hexane is the least selective and butane the most.

Increasing the solvent ratio from 1 to 2.5 produces the largest increase in selectivity. Increasing the hexane ratio from 1 to 2.5 at 100°C results in a reduction in asphaltenes from 18 to 12%. Pentane and butane show similar changes. Increasing the solvent ratio above 2.5 produces little change in the solvent selectivity as indicated by the relatively constant asphaltene values. However, at 150°C hexane selectivity appears to increase as the solvent ratio is increased above 2.5.

Because of the economic value of low boiling tar acids in tar processing, it was important to compare the solvents with respect to their ability to recover the tar acids boiling to 230°C. A comparison of the recovery of tar acids boiling to 230°C and the asphaltene carryover in the extract was made for propane, butane, pentane and hexane with the extraction temperature held constant at 100°C and the solvent ratio of 2.5, Figure 5. Recovery of tar acids boiling to 230°C increases with increased carbon chain length of the solvent. Thus, propane gives the lowest recovery, 23%, and hexane the highest, 69%. However, the higher boiling solvent shows a poorer selectivity by higher asphaltene carryover.

To determine if multi-stage extraction would increase the low boiling tar acid recovery, reject pitch from the one-stage extraction was contacted a second time with fresh solvent. The extraction was carried out at 100°C with pentane at a solvent ratio of 2.5. By this second extraction the total recovery of tar acids boiling to 230°C is increased to 78.5%. It is estimated that 5 stages are sufficient to give recoveries better than 95%.

Comparison of the ultimate analyses of extracts and pitches obtained at 100°C at a solvent ratio of 2.5 in Table I indicates that the more polar and hetero-atom compounds are preferentially rejected and concentrated in the pitch phase. The concentration of nitrogen, oxygen and sulfur is much lower in the extract. Compounds rich in hydrogen and the lower molecular weight compounds are concentrated in the extract. As the molecular weight of the solvent decreases, the selectivity for hydrogen rich components increases as evidenced by the increase in hydrogen content of the extracts. The selectivity for rejecting sulfur compounds is independent of solvent molecular weight.

Comparison of some of the properties of the extracts and rejects in Table II further shows the type of tar fractionation effected by the solvents. The extracts consist of the lower gravity, the higher hydrogen carbon ratio and lower viscosity tar components, that is, the lower molecular weight compounds. In passing from propane to hexane, each successively higher boiling solvent is fractionating the tar at some higher molecular weight cut point. This is borne out by the progressively increasing extract viscosity and increased softening point of the reject fraction.

A comparison of the fractional distillation analyses of the extracts shown in Figure 6 indicates that the solvents are fractionating the tar not only with respect to functional group components but also with respect to molecular weight or distillation cut point. As the carbon chain length of the solvent is increased, the distillation (analysis) of the extract approaches that of the feed tar. Thus, propane extract contains the least pitch (>350°C) and hexane extract the most. Since the amount of each distillate fraction boiling below the pitch fraction is greater than the corresponding feed tar fraction, it is indicative that solvent fractionation resembles fractional

distillation; however, the cut point corresponds to a higher temperature than obtainable by conventional fractional distillation. This cut point varies with the intrinsic solvent nature and increases with the increased boiling point of the paraffinic solvent employed. Thus, butane exhibits a higher cut point with respect to distillation than propane. Pentane is higher than butane, and the branched chain solvents behave more like the lower molecular weight straight chain analogues.

#### SUMMARY

1. An apparatus was designed which permitted extraction of a viscous tar with paraffinic hydrocarbon solvents over a range of temperatures with accurate phase separations and material balances.
2. Solvent ratios higher than 2.5 did not appreciably increase the yield of extract or extraction selectivity with solvents boiling above n-butane. Propane and n-butane differed from the higher boiling solvents in that yield of extract was proportional to the solvent and these solvents exhibited the highest selectivity.
3. Solvents boiling above n-butane showed higher yields but lower selectivity upon increasing the temperature. Normal butane extractions showed very little effect of temperature.
4. Extraction of low temperature tar was comparable to distillation in that, the higher molecular weight, higher boiling compounds were preferentially separated as a reject phase.
5. The depth of extraction, comparable to distillation cut point, was dependent upon the boiling point of the solvent employed. The higher the boiling point of the solvent the deeper was the cut point. The depth of extraction obtainable by solvents was at a higher molecular weight level than possible by conventional distillation.
6. High recovery of low boiling tar acids should be possible in a multi-stage extractor.

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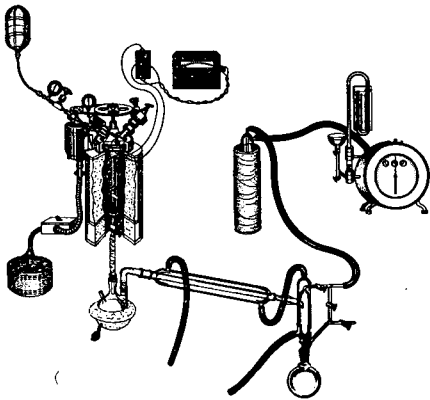


Figure 1

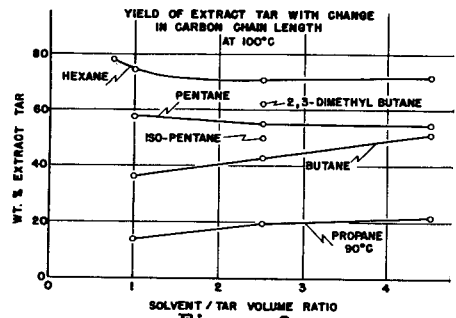


Figure 2

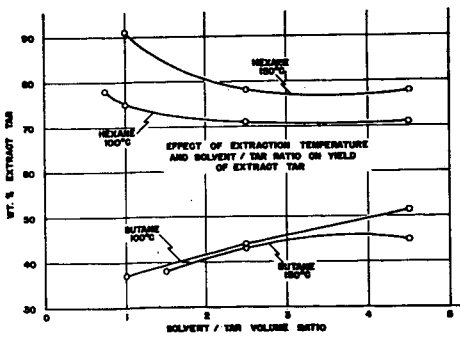


Figure 3

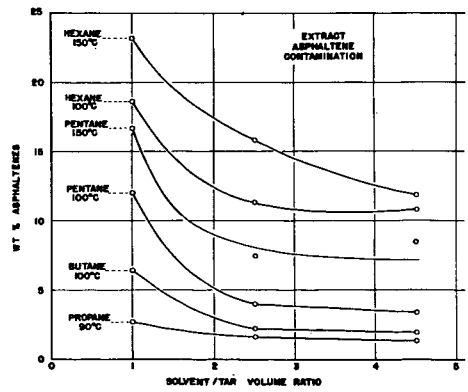


Figure 4

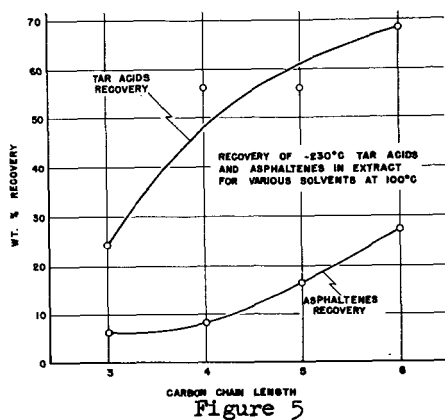


Figure 5

TABLE II

COMPARISON		OF PROPERTIES			
SOLVENT	FEED TAR	EXTRACTS			
		PROPANE	n-BUTANE	n-PENTANE	n-HEXANE
		<u>SOLUBLE FRACTION</u>			
SPEC. GRAY. 25/25°C	1.10	0.874	1.064	1.043	1.063
n/o	1.02	1.29	1.18	1.18	1.14
VISCOSITY S.U. SEC. 1000	1096	64.5	83.6	100.8	126.7
<u>REJECT FRACTION</u>					
FIXED CARBON		7.94	7.94	8.36	8.36
n/o	1.02	0.98	0.97	0.98	0.98
RED. V. GRAY. °		32.0	32.0	32.0	32.0

TABLE I

ULTIMATE ANALYSES					
SOLVENT	FEED TAR	EXTRACTS			
		PROPANE	n-BUTANE	n-PENTANE	n-HEXANE
<u>SOLUBLE FRACTION</u>					
H	7.09	9.17	8.40	8.29	8.07
C	82.89	84.98	84.86	85.51	84.39
N	0.87	0.20	0.39	0.49	0.46
O	6.76	4.96	5.49	4.85	6.42
S	1.18	0.75	0.76	0.86	0.66
<u>REJECT FRACTION</u>					
H		6.96	6.90	6.81	6.88
C		83.28	81.14	80.81	80.66
N		0.99	1.23	1.36	1.34
O		7.84	8.54	10.18	9.92
S		1.04	1.19	1.38	1.27

DISTILLATION OF EXTRACT TAR

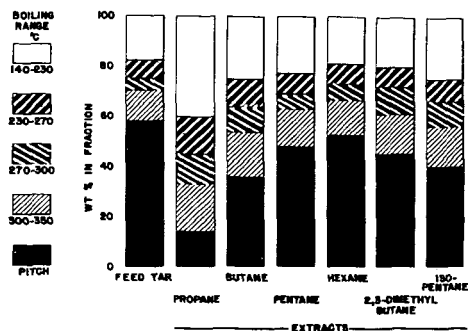


Figure 6

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American Chemical Society  
Boston, Massachusetts, Meeting, April 5-10, 1959

GAS-LIQUID CHROMATOGRAPHIC ANALYSIS OF AROMATIC HYDROCARBONS  
BOILING UP TO 218°C. IN A LOW-TEMPERATURE COAL TAR

Ta-Chuang Lo Chang and Clarence Karr, Jr.  
Low-Temperature Tar Laboratory  
Bureau of Mines  
U. S. Department of the Interior  
Morgantown, W. Va.

INTRODUCTION

Detailed analysis of low-temperature coal tar will lead to a clearer understanding of the chemical structure of the tar and thus help both in the study of the mechanism of carbonization and the development of uses for the tar.

As a part of a broad low-temperature coal tar characterization program, this paper presents the results of analysis of the aromatic hydrocarbons, boiling up to 218°C., which are present in the neutral oil portion of a low-temperature bituminous coal tar.

Previously only 28 aromatic hydrocarbons boiling between 80 - 218°C. were found in low-temperature bituminous coal tars by means of older analytical techniques<sup>1,2,3,4</sup>. In 1956 Grant and Vaughan<sup>5</sup> described the gas-liquid chromatographic analysis of aromatic hydrocarbons in coal tar naphthas, and identified benzofuran, an unspecified methyl styrene and six other aromatic hydrocarbons boiling up to 178°C. in two low-temperature coal tars; of these, only the methyl styrene was not previously reported.

In the present work, gas-liquid chromatography, together with other modern techniques, was used for analysis, and 52 aromatic hydrocarbons boiling up to 218°C. were found in a low-temperature bituminous coal tar, and their quantities determined.

A correlation was established between relative retention and boiling points for some alkyl benzenes, whereby the identification of several other aromatic hydrocarbons was made possible.

Besides indans, benzofurans, and indenenes, the aromatic hydrocarbons identified are methylated, ethylated, or propylated benzenes. Up to the present time, no butyl benzenes have been found in this particular tar.

Of the 52 compounds found, 27 had not been previously reported to be present in a low-temperature bituminous coal tar.

Another phase of the work concerning the analysis of higher boiling aromatic hydrocarbons such as biphenyls and alkyl naphthalenes, of which several have already been identified in this laboratory, is being completed and the results will be reported at a later date.

## EXPERIMENTAL WORK AND RESULTS

### I. Preparation of Aromatic Hydrocarbon Concentrates from the Coal Tar for Gas-Liquid Chromatography

#### Isolation of neutral oil from tar distillate

The tar used in this work was made from a West Virginia, Pittsburgh-seam, high-volatile bituminous coal in a fluidized carbonization pilot plant at about 480-510°C. The raw tar was de-ashed, dehydrated, and topped to about 175°C. at the plant. The tar distillate had been obtained in this laboratory under very mild temperature conditions calculated to be equivalent to about 350-360°C. at atmospheric pressure with a yield of 20.8 weight percent of the tar in the main distillate and less than 1 percent collected in a dry ice trap.

About three liters (2660 g.) of the main distillate were extracted according to the method of Fisher and Eisner<sup>6</sup> to remove tar acids and tar bases. The neutral oil thus obtained was washed three times with an equal volume of water. After passing it through a filter made of three layers of filter paper on a funnel, the oil was dried in a desiccator over anhydrous calcium chloride for a week. About 2400 ml. (2180 g.) of dry neutral oil, corresponding to 82% by weight of the distillate and 16.9% by weight of the tar, was obtained.

#### Fractional distillation of the neutral oil

A 698 g. charge of the neutral oil was fractionally distilled in a Podbielniak Hyper-Cal high-temperature automatic distillation apparatus. The column was 8 mm. by 36 inches and was packed with Heli-Grid Packing. The end point chosen for this distillation was a pot temperature of 200°C. to avoid any significant thermal alterations. The results of this distillation are given in Table I. Equivalent atmospheric boiling points were estimated from a standard nomograph.

#### Separation of the neutral oil fractions into chemical types by displacement chromatography

The silica gel adsorption method based on displacement chromatographic techniques which have been applied to petroleum distillates<sup>7</sup> and shale-oil naphthas<sup>8</sup> was adapted for separating the aromatic hydrocarbons from saturates and unsaturates.

The column chosen for this work consisted of an upper section 22 cm. long and 10 mm. I.D. and a lower section 138 cm. long and 3 mm. I.D. The entire column was jacketed to provide water for cooling or heating as required.

The column was packed with Davison Grade 950 silica gel, 60-200 mesh, which had been freshly activated at 160°C. for four hours just before packing. About 26 g. of silica gel were needed for the column. A fresh batch of silica gel was used for each run.

The sample was charged to the column, using about 3 p.s.i.g. oxygen-free nitrogen pressure. The desorbents selected were two different alcohols, the choice being made on the basis of the relative kinematic viscosities of the sample and the alcohol. An alcohol could be selected for each fraction so that its viscosity would be somewhat greater than that of the fraction. The alcohols were also chosen for desorbents on the basis of miscibility with the samples, and ease of removal from the last portions of the charge desorbed. After the sample was charged to the column, it was followed immediately by the desorbent with about 10 p.s.i.g. nitrogen pressure.

TABLE I  
FRACTIONATION OF NEUTRAL OILS IN PODBIEIŃIAK STILL

Charge: 16.92 wt. % of the tar  
698 g.  
Distillate: 360 g. = 51.6%  
Residue: 338 g. = 48.4%

Fraction no.	Head temp., °C., 50 mm.	Estimated b.p. °C., 760 mm.	Weight, g.
1	77.5 - 87.5	163 - 180	4.43
2	87.5 - 94.0		
3	94.0 - 101.4		
4	101.4 - 104.3	180 - 190	3.94
5	104.3 - 109.0	190 - 192	4.53
6	109.0 - 114.5	192 - 198	9.81
7	114.5 - 118.3	198 - 202	9.61
8	118.3 - 121.8	202 - 210	25.95
9	121.8 - 124.2		
10	124.2 - 126.5	210 - 213	5.29
11	126.5 - 130.9	213 - 220	17.88
12	130.9 - 132.9		
13	132.9 - 134.2	220 - 225	14.80
14	134.2 - 137.3	225 - 230	12.78
15	137.3 - 139.9	230 - 233	18.36
16	139.9 - 141.5	233 - 235	17.11
17	141.5 - 141.9	235 - 236	14.13
18	141.9 - 145.9	236 - 240	11.54
19	145.9 - 149.4	240 - 243	18.46
20	149.4 - 151.6	243 - 246	18.84
21	151.6 - 153.5	246 - 248	19.22
22	153.5 - 155.0	248 - 250	20.57
23	155.0	250	18.55
24	155.0 - 155.8	250 - 251	6.34
25	155.8 - 157.8	251 - 253	18.46
26	157.8 - 158.0	253 - 253	18.46
27	158.0 - 159.9	253 - 254	18.07
28	159.9 - 162.0	254 - 256	21.34
29	162.0 - 163.0	256 - 260	11.53
Total			360.00

The operating temperature chosen for each sample depended on the melting points of the expected components in the fraction. If some of them were crystalline at room temperature, a temperature near the melting points of the components was used.

Fractions were obtained with an automatic fraction collector which counted drops photoelectrically and maintained the fractions in an atmosphere of oxygen-free nitrogen.

Usually only the very last fraction was contaminated by the desorbent. The desorbent was removed by extracting with 80 to 90% glycerine, and the glycerine was then removed with several water washings. The alcohol- and glycerine-free sample was dried overnight over anhydrous calcium chloride in a partially evacuated desiccator. The refractive index was obtained on each fraction, and by comparing these values with literature values for pure hydrocarbons in the boiling range of the charge, it was readily estimated where the paraffins and naphthenes, olefins, aromatics, and neutral oxygen, nitrogen and sulfur compounds were located among the fractions. With this technique, no sharp border lines could be expected between two adjacent types. However, it was found that overlapping occurred only in the very first and the very last fractions of any one type.

Since this paper covers the first six distillate fractions, boiling from 163° - 202°C., the data on displacement chromatography for only these fractions are given in Table II. About 17 drops per displacement fraction were collected, except for the last one, which consisted of about 50 drops.

## II. Analysis of Aromatic Hydrocarbons by Gas-Liquid Chromatography

### Apparatus and operating conditions

A Perkin-Elmer Model 154C Vapor Fractometer was used. The response range of the recorder was 0-11 millivolts and the speed of the chart was 3.75 in./hr. The peak areas produced by components of the sample on the chromatogram were measured with a planimeter.

The column for this work was made from a 15 ft. x  $\frac{1}{4}$  in. O.D. copper tubing filled with approximately 50 g. of packing made of 25% Apiezon L grease on 30-60 mesh fire brick. After packing, the column was coiled to fit into the column chamber of the Fractometer.

The temperature chosen for the analysis was 150°C., approximately 10°C. below the lowest boiling fraction and 50°C. below the highest boiling fraction. Samples were injected with 10 or 50 microliter syringes. The carrier gas was helium, admitted to the column at a pressure of 12 lb./in.<sup>2</sup>, corresponding to a flow rate of 95 ml./min. The outlet pressure was atmospheric. The voltage for the bridge of the thermoconductivity detector was 8 volts and the most sensitive range was used. Throughout the work, the temperature stayed within  $\pm 0.1^\circ\text{C}$ . and the carrier gas pressure and the voltage of the bridge stayed constant.

The efficiency of the column under these conditions, referring to n-propylbenzene and to 1,2,3,5-tetramethylbenzene, was 3520 and 3885 theoretical plates, respectively, calculated by using the equation<sup>9</sup>, No. of theoretical plates =  $16(x/y)^2$ , where y = length of peak base line (as defined), and x = length from start of run to middle of base line section.

TABLE II  
DISPLACEMENT CHROMATOGRAPHIC SEPARATION OF NEUTRAL OIL DISTILLATE FRACTIONS INTO CHEMICAL TYPES

Distillate fraction no.	1 + 2	3	4	5	6
Weight of charge, g.	1.77	3.15	3.60	7.40	7.70
Desorbent	Isopropyl alcohol	Isopropyl alcohol	Isopropyl alcohol	Isopropyl alcohol	Butyl alcohol
Saturates + some olefins					
Number of fractions	5	3	4	7	5
Refractive index range, $n_D^{20}$	1.3930-1.3941	1.4381-1.4832	1.4252-1.4471	1.4328-1.4695	1.4400-1.4683
Total weight, g.	0.74	0.61	1.20	2.11	1.93
Aromatics + some olefins + some O,S compounds					
Number of fractions	4	5	5	9	12
Refractive index range, $n_D^{20}$	1.3941-1.5007	1.4832-1.5310	1.4911-1.5397	1.4912-1.5545	1.4895-1.5601
Total weight, g.	0.70	2.29	2.17	4.32	5.21
N, S, and O compounds retained on column	0.33 g.	0.25 g.	0.23 g.	0.97 g.	0.56 g.
Weight of aromatic hydrocarbons identified by GLC	0.57 g.	1.95 g.	1.66 g.	4.30 g.	4.81 g.

#### Sample collecting system for gas-liquid chromatography

The original fraction collecting system for the Perkin-Elmer instrument has a short length of 1/8 in. stainless-steel tubing leading from the detector cell to an external syringe needle adaptor that has a 3-way syringe valve. This is intended for attaching a short needle which can be inserted through a rubber serum bottle cap at the bottom of a solvent-filled tube for washing effluent gas in order to collect fractions. However, this type of collector was found to be unsatisfactory in most cases.

A new fraction collecting system was devised, which would take advantage of the existing needle adaptor. This involved heating the stainless-steel tubing electrically to prevent the fractions from condensing, and using 6 inch-18 gauge syringe needles cooled with powdered dry ice as fraction collectors. Holders for dry ice powder were made from 110 mm. lengths of 18 mm. O.D. glass tubing, which were wrapped with aluminum foil and asbestos string, and plugged at one end with 12 mm. thick cork stoppers, each having a small hole in the center for entry of the needles. To collect the material producing a chromatogram peak, one of the needles was fastened to the upright needle adapter and one of the dry ice jackets was slipped down over the needle, the insulating cork plug resting on the hot needle hub. The jacket was carefully packed with dry ice powder and the 3-way valve turned to admit effluent gas to the needle. After collecting a sample, the needle was removed, a Teflon plug inserted at the hub end and a little polyethylene tube slipped over the needle end, and placed in a dewar flask containing dry ice. The infrared spectrum of the sample was subsequently obtained in a 0.05 mm. or 0.1 mm. microcell for identification of the components. The infrared microcell was filled by inserting the needle tip into the cell and introducing a fraction of a drop of carbon disulfide into the needle hub. However, in some instances, it was necessary to wash out the needle with about 1/2 ml. carbon disulfide, collecting the solution in a 1-ml. beaker and carefully evaporating off solvent with a gentle stream of nitrogen until about one drop of solution remained. This was then placed into the microcell by capillary action, using the capillary tubing of the cell. Good infrared spectra were obtained with about 1-mg. hydrocarbon, and, in particular, there was no contamination from compounds producing adjacent peaks.

#### General approach for identification

The retention times of 42 aromatic hydrocarbons boiling in the range of the neutral oil samples were obtained, for the purpose of preliminary identification of the unknowns. The relative retentions at 150°C. and 200°C. of the 42 aromatics, referred to n-propylbenzene, are shown in Table III. These relative retention values can be considered to be either relative retention times or relative retention volumes.

The aromatic fractions obtained by displacement chromatography of the first six distillate fractions were individually examined by gas-liquid chromatography under the same conditions for the known compounds. To confirm the identification, the material producing each peak was collected for infrared spectrophotometric analysis. Three methods were used to identify the aromatic hydrocarbons present in the fractions.

The first method of identification consisted of a combination of conventional gas-liquid chromatography and infrared spectrophotometry. The retention times of unknown peaks were compared with those of known compounds for a preliminary identification. The material producing each peak was then collected in a microcell for an infrared spectrum, as previously described. The confirmation of identity was then made by comparing this spectrum with that of the known compound.

TABLE III

LITERATURE BOILING POINTS, RELATIVE RETENTIONS AND CALIBRATION  
FACTORS ( $f_c$ ) OF SOME AROMATIC HYDROCARBONS

Compound	Literature b.p. °C., 760 mm. <sup>a</sup>	Relative <sup>b</sup> retention (150°C.)	$f_c$ (150°C.) <sup>c</sup>	Relative <sup>b</sup> retention (200°C.)
Methylbenzene	110.626	0.36	1.02	0.48
Ethylbenzene	136.186	0.62	0.95	0.64
1,4-Dimethylbenzene	138.351	0.67	0.98	0.70
1,3-Dimethylbenzene	139.104	0.68	1.00	0.71
1,2-Dimethylbenzene	144.411	0.77	1.01	0.82
Isopropylbenzene	152.392	0.83	1.02	0.86
n-Propylbenzene	159.217	1.00	1.00	1.00
1-Methyl-3-ethylbenzene	161.305	1.06	1.01	—
1-Methyl-4-ethylbenzene	161.989	1.09	1.08	1.06
1-Methyl-2-ethylbenzene	165.153	1.21	1.06	1.17
1,3,5-Trimethylbenzene	164.716	1.19	1.08	1.13
1,2,4-Trimethylbenzene	169.351	1.38	1.03	1.29
1,2,3-Trimethylbenzene	176.084	1.67	1.04	1.52
Indan	177.82	1.82	1.65	1.69
Isobutylbenzene	172.759	1.33	1.07	1.26
sec-Butylbenzene	173.305	1.34	1.08	1.27
n-Butylbenzene	183.27	1.77	1.04	1.56
1-Methyl-3-isopropylbenzene	175.14	1.39	1.07	1.27
1-Methyl-4-isopropylbenzene	177.10	1.48	1.04	1.35
1-Methyl-2-isopropylbenzene	178.15	1.58	0.94	1.42
1-Methyl-3-n-propylbenzene	181.80	1.71	1.03	1.51
1-Methyl-4-n-propylbenzene	183.30	1.76	1.03	1.58
1-Methyl-2-n-propylbenzene	184.80	1.90	1.07	1.67
1,3-Diethylbenzene	181.102	1.62	1.00	1.45
1,2-Diethylbenzene	183.423	1.81	1.06	1.60
1,4-Diethylbenzene	183.752	1.79	1.03	1.58
1,3-Dimethyl-5-ethylbenzene	183.75	1.82	1.09	1.59
1,2,4,5-Tetramethylbenzene	196.80	2.77	0.93	2.28
1,2,3,5-Tetramethylbenzene	198.00	2.87	1.06	2.33
Indene	182.44	1.92	1.10	1.80

(Table III Continued)

Compound	Literature b.p. °C., 760 mm. <sup>a</sup>	Relative <sup>b</sup> retention (150°C.)	$f_c$ (150°C.) <sup>c</sup>	Relative <sup>b</sup> retention (200°C.)
1-Methylindene	199	2.22	1.20	1.98
2-Methylindene	208	3.48	1.15	2.96
1-Methyl-3,5-diethylbenzene	200.70	2.68	1.11	2.14
1,2,3,4-Tetrahydronaphthalene	207.57	3.84	2.05	3.13
1,4-Diisopropylbenzene	208.9	3.26	—	2.49
1,2-Diisopropylbenzene	209	3.06	—	2.51
Benzofuran	171.38	1.35	1.15	1.33
Naphthalene	217.96	4.68	1.14	3.51
1,3,5-Triethylbenzene	216.2	3.87	—	1.13
Pentamethylbenzene	231.8	7.08	—	4.87
$\beta$ -Methylstyrene (trans)	178.26	1.64	1.09	1.47
$\alpha$ -Methylstyrene	165.5	1.22	1.11	1.14
1,4-Dimethyl-2-ethylbenzene	186.91	2.04 <sup>d</sup>	—	1.73 <sup>d</sup>
1,2-Dimethyl-4-ethylbenzene	189.75	2.17 <sup>d</sup>	—	1.89 <sup>d</sup>
1-Methylindan	190.6	2.30 <sup>d</sup>	—	1.99 <sup>d</sup>
1,2-Dimethyl-3-ethylbenzene	193.91	2.50 <sup>d</sup>	—	2.06 <sup>d</sup>
5-Methylindan	202.0	3.25 <sup>d</sup>	—	2.67 <sup>d</sup>
1-Methyl-3,4-diethylbenzene	203.6	3.00 <sup>d</sup>	—	—
4-Methylindan	205.5	3.46 <sup>d</sup>	—	2.81 <sup>d</sup>
1,2,3,4-Tetramethylbenzene	205.04	3.48 <sup>d</sup>	—	2.81 <sup>d</sup>
3-Methylindene	205	3.50 <sup>d</sup>	—	2.82 <sup>d</sup>

<sup>a</sup> All values, except for benzofuran, from API Research Project 44, "Selected Values of Properties of Hydrocarbons and Related Compounds," Carnegie Institute of Technology, Pittsburgh, Pa. Benzofuran b.p. from J. N. Breston and A. W. Gauger, Proc. Am. Gas Assoc., 28 (1946) 492.

<sup>b</sup> Dead volume corrected.

<sup>c</sup> Defined in eq. 1.

<sup>d</sup> The relative retentions of these compounds were determined from tar components identified by I.R.

Retention times could not, of course, be obtained for those compounds for which authentic specimens were not available. A second method of identification was used for these compounds which involved the correlation curves of relative retentions and boiling points shown in Fig. 2 and explained in detail in a later section. Boiling points of the unknowns producing peaks were obtained from their relative retentions by these correlation curves, and were used as a preliminary means of identification. Since literature infrared spectra of a number of compounds were available, confirmation could be made in these instances.

For a third group of compounds, neither the retention times nor the infrared spectra of authentic specimens were available. However, from the correlation curves and the relative retentions of the unknown peaks, tentative identification could be made through the boiling points. Also by correlating infrared absorption bands and molecular structures, these tentative identities could be further substantiated.

To illustrate the first and second methods of identification, the chromatogram of a typical fraction is shown in Fig. 1, and the boiling points of the components producing the peaks, as obtained from the correlation curves, are presented in Table IV. Excellent agreement is shown between literature and predicted boiling points. The peak numbers in Fig. 1 are explained in Table IV. This chromatogram was produced by a 10 $\mu$ l. sample of an aromatic cut of  $n_D^{20} = 1.5074$ , from distillate fraction no. 5 in a boiling range of 192-198°C.

TABLE IV

IDENTIFICATION OF COMPONENTS PRODUCING ELUTION PEAKS IN THE GLC  
OF AN AROMATIC CUT FROM DISTILLATE FRACTION NO. 5

Peak no.	Relative retention	Compound identified	Relative retention of known compound	Boiling point. °C.	
				Literature	From correlation curve
1	1	n-Propylbenzene (added standard)	1	159.2	159.2
2	1.69	1-Methyl-3-n-propylbenzene	1.71	181.8	181.3
3	1.82	1,3-Dimethyl-5-ethylbenzene	1.82	183.8	183.5
4	1.89	1-Methyl-2-n-propylbenzene	1.90	184.8	184.8
5	2.02	1,4-Dimethyl-2-ethylbenzene	*	186.9	186.9
6	2.16	1,2-Dimethyl-4-ethylbenzene	*	189.8	189.1
7	2.29	1-Methylindan	*	190.6	191.0
8	2.46	1,2-Dimethyl-3-ethylbenzene	*	193.9	193.5
9	2.65	1-Methyl-3,5-diethylbenzene	2.68	200.7	200.7
10	2.79	1,2,4,5-Tetramethylbenzene	2.77	196.8	197.3
11	2.86	1,2,3,5-Tetramethylbenzene	2.87	198.0	198.2
12	3.00	1-Methyl-3,4-diethylbenzene	*	203.6	204.2
13	3.25	5-Methylindan	*	202.0	202.3
14	3.45	4-Methylindan	*	205.5	204.3

\* Authentic specimens not available for determination of retention times.

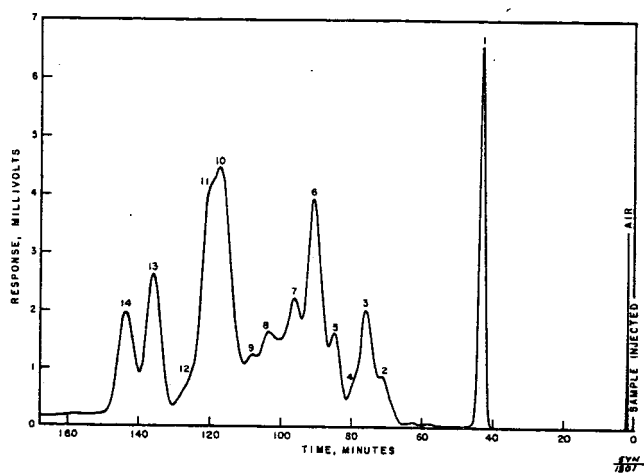


Fig. 1. Chromatogram of an aromatic cut obtained from distillate fraction no. 5.

Peak 1 is produced by n-propylbenzene, the internal standard, added to the cut for quantitative estimation of the components. The components producing peaks 2, 3, 4, 9, 10 and 11 were identified by comparing the retention times with those of known compounds. The components producing peaks 5, 6, 7, 8, 12, 13 and 14 were identified through their boiling points, obtained from their relative retention and the correlation curves. To confirm the identities, a 25  $\mu$ l.-sample was used to produce enough material for each major peak for infrared spectrophotometric analysis. However, the minor ones, such as 4, 8, 9 and 12, were better confirmed by the infrared spectra of the material producing the corresponding peaks in the chromatogram of an adjacent aromatic cut.

Table V illustrates the third method of identification. It is to be noted that the identities of three compounds were further substantiated by considering the infrared absorption bands and probable molecular structures according to the correlations of Bellamy<sup>10</sup>. Two compounds were present in the last two distillate fractions (no. 5 and no. 6) in such small quantities that no satisfactory infrared spectra were obtained. Infrared spectra were obtained, however, for the components producing all the significant chromatogram peaks. It was observed that only a few weak absorption bands were unaccounted for by the compounds identified. The relative intensities of these bands were such that these unknown components could have been present in only trace amounts.

#### Quantitative estimation of aromatic hydrocarbons

The internal standard method was adapted for quantitative analysis of the samples, n-propylbenzene being selected as the standard. Keulemans, Kwantes and Rijnders<sup>11</sup> have demonstrated the use of an average calibration factor,  $f_c$ , defined as follows, for calibrating areas and percentages for a component, and an internal standard for obtaining precise quantitative analysis of light hydrocarbons:

$$f_c = A_s W_c / A_c W_s \quad (1)$$

where  $A_s$  and  $A_c$  are the areas for the internal standard and component in the mixture, and  $W_c$  and  $W_s$  are the weight percentages of the component and the standard.

In order to investigate the deviation of the average calibration factors of aromatic hydrocarbons from the actual values in a certain range of concentrations, eight pure compounds, namely, 1-methyl-3-ethylbenzene, 1,3,5-trimethylbenzene, indan, 1,3-diethylbenzene, indene, 1,3-dimethyl-5-ethylbenzene, 1,2,3,5-tetramethylbenzene, and 1,2,3,4-tetrahydronaphthalene, were used. Three solutions of each compound in different concentrations, about 15%, 30%, and 60% by weight, were prepared in n-propylbenzene. Using these 24 solutions, the  $f_c$  values were then calculated from the weight percentages and the peak areas produced by the components in their chromatograms. It was found that the average  $f_c$  in the concentration range of 15-60% by weight had a maximum deviation of only about  $\pm 3\%$  from the actual values, and the best results were obtained at concentration ranges of 30-60%. This is considered accurate enough for estimating the amounts of aromatic components present in such a complex mixture as coal tar. The  $f_c$  values for the rest of the aromatic hydrocarbons were determined only once at 150°C. at a concentration of 40-50%. These  $f_c$  values are shown in Table III and were used to determine the weight percentages of all aromatic hydrocarbons in the fractions. For those compounds which were not available in this laboratory but found to be present in the sample, the  $f_c$  value of its isomers or of a structurally similar compound was used.

Two synthetic blends were analyzed by using these  $f_c$  values and the results are shown in Table VI.

TABLE V

## DATA FOR TENTATIVE IDENTIFICATION OF FIVE ALKYL BENZENES

Name of compound	Literature b.p., °C., 760 mm.	Relative retention of the unknown peak	B.p., °C., obtained from the correlation curve	Infrared spectral-structural correlations
1,4-Dimethyl-2-isopropylbenzene	196.2	2.38	196.8	—
1,3-Dimethyl-2-n-propylbenzene	207.6	3.35	207.8	—
1,4-Dimethyl-2-n-propylbenzene	203.6	3.04	203	12.23 $\mu$ (S): 2H out-of-plane deformation vibration 11.39 $\mu$ (M): 1H out-of-plane deformation vibration 9.12 $\mu$ (W); 9.47 $\mu$ (W); 9.90 $\mu$ (MW) suggest 1,2,4-substitution of benzene ring Probable structure: 1,2,4- trialkylbenzene
1-Methyl-2,4-diethylbenzene	205.0	3.10	205.3	12.40 $\mu$ (S): 2H out-of-plane deformation vibration 11.30 $\mu$ (M): 1H out-of-plane deformation vibration 9.60 $\mu$ (W); 9.70 $\mu$ (W); and 8.65 $\mu$ (W) suggest 1,2,4-substitution of benzene ring Probable structure: 1,2,4- trialkylbenzene
1,2-Dimethyl-3-n-propylbenzene	210.7	3.64	210.5	12.81 $\mu$ (S) and 14.32 $\mu$ (M): 3H out- of-plane deformation vibration 8.67 $\mu$ (W): 1,2,3-substitution of benzene ring Probable structure: 1,2,3- trialkylbenzene

TABLE VI  
ANALYSIS OF SYNTHETIC BLENDS

Blend	Component	Relative retention	Wt. % present	Wt. % found		
				Run 1	Run 2	Run 3
A	Isopropylbenzene	0.82	10.28	10.31	10.47	10.77
	n-Propylbenzene	1.00	11.67	—	—	—
	1,3,5-Trimethylbenzene	1.29	12.93	12.91	12.82	12.61
	1-Methyl-2-isopropylbenzene	1.56	12.62	12.14	12.16	12.54
	Indan	1.82	19.07	18.08	18.60	18.34
	Indene	1.92	14.71	15.03	15.05	14.67
	1,2,3,5-Tetramethylbenzene	2.88	18.72	19.16	19.19	18.66
	Total		100.00	99.30	99.96	99.26
B	n-Propylbenzene	1.00	14.64	—	—	—
	sec-Butylbenzene	1.35	18.14	17.62	17.42	—
	1-Methyl-4-isopropylbenzene	1.48	15.23	14.91	14.97	—
	1-Methyl-3-n-propylbenzene	1.72	17.07	16.97	17.09	—
	1,3-Dimethyl-5-ethylbenzene	1.84	21.37	21.28	21.54	—
	1-Methylindene	2.23	13.64	13.54	13.76	—
	Total		100.00	98.96	99.42	—

For analyzing the components in the sample, a certain amount of the internal standard, n-propylbenzene, roughly 15% by weight, was added to each of the sample fractions so that the peak area of the standard was approximately equal to that of the major peaks. A new chromatogram of each fraction, after the addition of the standard, was then made. The percentage of each component was then calculated by using equation (1). In the few instances of unresolved components, conventional quantitative infrared analysis was used.

The aromatic hydrocarbons found in the low-temperature bituminous coal tar and their quantities are presented in Table VII. The values of wt. % in neutral oil for the highest boiling components are not entered, since it is expected that more of these compounds will be found in distillate fractions 7 and 8.

#### DISCUSSION

##### Correlation between relative retention and boiling points of alkylbenzenes having an equal number of carbon atoms

Desty and Whyman<sup>12</sup> plotted the boiling points of a large number of low-boiling paraffinic hydrocarbons and a few aromatic hydrocarbons against the logarithm of their relative retention volumes for two different stationary phases, resulting in two almost straight lines for each of the solvents. These plots indicate the selectivity of the two stationary phases for these two different types of solutes and offer help in choosing a suitable solvent for the separation of these two general types. However, no relationship between the relative retentions and boiling points of alkylbenzenes having an equal number of carbon atoms in the alkyl group has ever been expressed for the purpose of identifying this type of hydrocarbon. When the logarithms of relative retention for alkylbenzenes with an equal number of carbon atoms in the alkyl group were plotted against their boiling points, a straight line resulted. Fig. 2 shows five such lines corresponding to alkylbenzenes having 2, 3, 4, 5, and 6 carbon atoms in the alkyl groups. It is interesting to see that these lines are parallel to each other. There is a similar correlation at 200°C.

TABLE VII

ANALYSIS OF INDIVIDUAL AROMATIC HYDROCARBONS BOILING UP TO 200°C.  
IN NEUTRAL OIL DISTILLATE FRACTIONS

Compounds identified	Fractions	Method of identification	Source of I.R. spectrum	Total wt., g.	Wt. % in neutral oil <sup>a</sup>
Methylbenzene <sup>b</sup>	1,2	Rel. retention	—	1 <sup>c</sup>	Trace
Ethylbenzene <sup>b</sup>	1,2	Rel. retention	—	2 <sup>c</sup>	Trace
1,3- and 1,4-Dimethylbenzene <sup>b</sup>	1,2	Rel. retention	—	9 <sup>c</sup>	Trace
1,2-Dimethylbenzene <sup>b</sup>	1,2	Rel. retention	—	20 <sup>c</sup>	Trace
Isopropylbenzene <sup>b</sup>	1,2	Rel. retention	—	79 <sup>c</sup>	Trace
n-Propylbenzene <sup>b</sup>	1,2	Rel. retention, I.R.	d	250 <sup>c</sup>	0.002
1-Methyl-3-ethylbenzene <sup>b</sup>	1,2	Rel. retention, I.R.	e	0.010	0.001
1-Methyl-4-ethylbenzene <sup>b</sup>	1,2	Rel. retention, I.R.	e	0.0098	0.001
1-Methyl-2-ethylbenzene <sup>b</sup>	1,2	Rel. retention, I.R.	e	0.0075	0.001
1,2,3-Trimethylbenzene <sup>b</sup>	1,2	Rel. retention, I.R.	e	0.3105	0.045
1,2,4-Trimethylbenzene <sup>b</sup>	1,2,3	Rel. retention, I.R.	e	0.2695	0.039
1,3,5-Trimethylbenzene <sup>b</sup>	1,2,3	Rel. retention, I.R.	e	0.1184	0.017
1-Methyl-4-isopropylbenzene	1,2,3,4	Rel. retention, I.R.	d	0.0596	0.009
1-Methyl-3-isopropylbenzene	1,2,3,4	Rel. retention, I.R.	d	0.0511	0.007
1-Methyl-2-isopropylbenzene	3	Rel. retention, I.R.	d	0.0164	0.002
1,2-Diethylbenzene	3,4	Rel. retention, I.R.	e	0.0857	0.012
1,3-Diethylbenzene	3,4	Rel. retention, I.R.	e	0.1009	0.015
1,4-Diethylbenzene <sup>b</sup>	4	Rel. retention	—	0.0062	0.001
1,2-Dimethyl-4-ethylbenzene <sup>b</sup>	3,4,5,6	Rel. retention- b.p. correlation, I.R.	e	1.8139	0.260
1,4-Dimethyl-2-ethylbenzene	3,4,5,6	Rel. retention- b.p. correlation, I.R.	e	0.7698	0.110

(Table VII Continued)

<u>Compounds identified</u>	<u>Fractions</u>	<u>Method of identification</u>	<u>Source of I.R. spec-trum</u>	<u>Total wt.,g.</u>	<u>Wt. % in neutral oil<sup>a</sup></u>
1,3-Dimethyl-5-ethylbenzene <sup>b</sup>	3,4,5,6	Rel.retention,I.R.	d	1.0872	0.156
1,2-Dimethyl-3-ethylbenzene <sup>b</sup>	4,5,6	Rel. retention-b.p. correlation, I.R.	e	0.5938	0.085
1-Methyl-3-n-propylbenzene	3,4,5	Rel.retention,I.R.	d	0.3180	0.046
1-Methyl-2-n-propylbenzene	5	Rel.retention,I.R.	d	0.0753	0.011
1,2,4,5-Tetramethylbenzene <sup>b</sup>	4,5,6	Rel.retention,I.R.	d	1.1066	0.159
1,2,3,5-Tetramethylbenzene	5,6	Rel.retention,I.R.	d	1.7690	0.253
1,2,3,4-Tetramethylbenzene <sup>b</sup>	6	Rel. retention-b.p. correlation, I.R.	e	0.8852	—
Indene <sup>b</sup>	1,2,3,4	Rel.retention,I.R.	e	0.2331	0.033
3-Methylindene	5,6	I.R.	e	0.5378	—
Indan <sup>b</sup>	1,2,3	Rel.retention,I.R.	d	0.3945	0.057
1-Methylindan	3,4,5,6	Rel. retention-b.p. correlation, I.R.	f	1.1265	0.161
5-Methylindan	5,6	Rel. retention-b.p. correlation, I.R.	f	1.4976	—
4-Methylindan <sup>b</sup>	5,6	Rel. retention-b.p. correlation, I.R.	f	1.4988	—
1,3-Dimethyl-2-n-propylbenzene	5	Rel. retention-b.p. correlation	—	0.0173	0.003
1,2-Dimethyl-3-n-propylbenzene	5,6	Rel. retention-b.p. correlation, I.R.-structural correlation	—	0.1008	—
1,4-Dimethyl-2-n-propylbenzene	5,6	Rel. retention-b.p. correlation, I.R.-structural correlation	—	0.4124	—

(Table VII Continued)

Compounds identified	Fractions	Method of identification	Source of I.R. spec-trum	Total wt., g.	Wt. % in neutral oil <sup>a</sup>
1,4-Dimethyl-2-isopropylbenzene <sup>b</sup>	5	Rel. retention-b.p. correlation	—	0.1151	0.017
1-Methyl-3,5-diethylbenzene	5,6	Rel. retention, I.R.	d	0.2393	0.034
1-Methyl-2,4-diethylbenzene	6	Rel. retention-b.p. correlation, I.R.-structural correlation	—	0.6505	—
Styrene	1,2	I.R.	g	0.0332	0.005
4-Methylstyrene	1,2	I.R.	h	0.0225	0.003
<i>β</i> -Methylstyrene (trans)	1,2	Rel. retention, I.R.	d	0.1396	0.020
3-Phenyl-1-butene	1,2	I.R.	g	0.1163	0.017
1,2,3,4-Tetrahydronaphthalene	5,6	Rel. retention, I.R.	d	0.3171	—
Naphthalene <sup>b</sup>	6	I.R.	d	0.0886	—
Benzofuran <sup>b</sup>	1,2	Rel. retention, I.R.	d	0.0991	0.014
5-Methylbenzofuran	3	I.R.	g } g }	0.1432	0.021
6-Methylbenzofuran	3,4	I.R.			
2-Methylbenzofuran	4	I.R.	g } g }	0.1681	0.024
3-Methylbenzofuran	4	I.R.			
7-Methylbenzofuran	3,4	I.R.	g	0.0785	0.011

<sup>a</sup> Total neutral oil distilling up to about 360°C., representing 16.92 wt. % of the total tar.

<sup>b</sup> Previously identified by others<sup>1,2,3,4,5</sup>.

<sup>c</sup> Ratio to methylbenzene.

<sup>d</sup> This laboratory.

<sup>e</sup> American Petroleum Institute, Research Project 44, infrared spectral data, Carnegie Institute of Technology, Pittsburgh, Pa.

<sup>f</sup> Jacob Entel, Clarence H. Rouf, and H. C. Howard, *Anal. Chem.* **25** (1953) 1303.

<sup>g</sup> Samuel P. Sadtler & Son, Inc., Philadelphia, Pa.

<sup>h</sup> Courtesy of W. F. Hammer, Monsanto Chemical Co., Texas City, Texas.

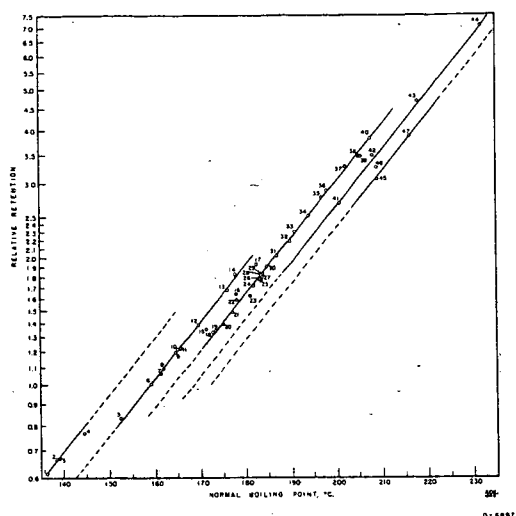


Fig. 2. Correlation between relative retentions and boiling points of some aromatic hydrocarbons at 150°C. on Apiezon I grease.

Legend:

- |                                |                                  |
|--------------------------------|----------------------------------|
| 1 Ethylbenzene                 | 25 1-Methyl-4-n-propylbenzene    |
| 2 1,4-Dimethylbenzene          | 26 n-Butylbenzene                |
| 3 1,3-Dimethylbenzene          | 27 1,4-Diethylbenzene            |
| 4 1,2-Dimethylbenzene          | 28 1,2-Diethylbenzene            |
| 5 Isopropylbenzene             | 29 1,3-Dimethyl-5-ethylbenzene   |
| 6 n-Propylbenzene              | 30 1-Methyl-2-n-propylbenzene    |
| 7 1-Methyl-3-ethylbenzene      | 31 1,4-Dimethyl-2-ethylbenzene   |
| 8 1-Methyl-4-ethylbenzene      | 32 1,2-Dimethyl-4-ethylbenzene   |
| 9 1,3,5-Trimethylbenzene       | 33 1-Methylindan                 |
| 10 1-Methyl-2-ethylbenzene     | 34 1,2-Dimethyl-3-ethylbenzene   |
| 11 $\alpha$ -Methylstyrene     | 35 1,2,4,5-Tetramethylbenzene    |
| 12 1,2,4-Trimethylbenzene      | 36 1,2,3,5-Tetramethylbenzene    |
| 13 1,2,3-Trimethylbenzene      | 37 5-Methylindan                 |
| 14 Indan                       | 38 4-Methylindan                 |
| 15 Benzofuran                  | 39 1,2,3,4-Tetramethylbenzene    |
| 16 $\beta$ -Methylstyrene      | 40 1,2,3,4-Tetrahydronaphthalene |
| 17 Indene                      | 41 1,3-Diethyl-5-methylbenzene   |
| 18 Isobutylbenzene             | 42 2-Methylindene                |
| 19 sec-Butylbenzene            | 43 Naphthalene                   |
| 20 1-Methyl-3-isopropylbenzene | 44 Pentamethylbenzene            |
| 21 1-Methyl-4-isopropylbenzene | 45 1,2-Diisopropylbenzene        |
| 22 1-Methyl-2-isopropylbenzene | 46 1,4-Diisopropylbenzene        |
| 23 1,3-Diethylbenzene          | 47 1,3,5-Triethylbenzene         |
| 24 1-Methyl-3-n-propylbenzene  |                                  |

Indans and tetralin, which have a benzene nucleus and a fused saturated ring, fall closely on the correlation curves for alkylbenzenes with the corresponding number of carbon atoms in the alkyl group and, therefore, are included in these series. Indenes, styrenes, and naphthalene which have a double bond in the "side chain," however, do not follow the corresponding curves and appear to have a different pattern. From the limited data obtained at present, no correlation can be found for these types.

These correlation curves can be expressed by the following empirical equation:

$$\log V_R = mT_B - c \quad (2)$$

where  $V_R$  = relative retention of an alkyl benzene,  
 $T_B$  = normal boiling point of the compound, °C.,  
 $m$  = slope,  
 $c$  = Y - intercept at any temperature; 0°C. arbitrarily selected.

The slope for the set of five alkylbenzene series at 150°C. on a stationary phase of Apiezon L grease is 0.0135, and their intercepts on the vertical axis at 0°C. are 2.0496, 2.1442, 2.2154, 2.2760, and 2.3215 for alkylbenzenes with 2, 3, 4, 5, and 6 carbon atoms in the alkyl group. The values of the intercept  $c$  are, of course, a measure of the separation of the five parallel lines from each other.

The intercept  $c$  in eq. 2 can be correlated with the number of carbon atoms in the alkyl group,  $N_C$ , as shown in Fig. 3. This can be expressed as follows:

$$\log N_C = a \log c - b \quad (3)$$

where  $N_C$  = number of carbon atoms in the alkyl group,  
 $a$  = slope,  
 $b$  = intercept.

For the curve shown in Fig. 3,  $a = 8.78$  and  $b = 2.431$ .

From eq. 3, it is possible to generate a family of relative retention-boiling point curves when only one is known.

The relationship between relative retentions and boiling points of alkylbenzenes was found to be very useful for characterization. For example, peak 6 in the chromatogram shown in Fig. 1 has a relative retention of 2.16. By checking the curves in Fig. 2, it was readily determined that the boiling point of this unknown in a distillate fraction boiling at about 192-198°C. should be 189.3°C. if it is an alkylbenzene having four carbons in the alkyl group or 193.8°C. if it has an alkyl group of five carbon atoms. 1,2-Dimethyl-4-ethylbenzene boils at 189.79°C. and 1-methyl-3-isobutyl- and 1-methyl-3-sec-butylbenzene both boil at 194°C. The infrared spectrum of the collected material producing this peak agreed very well with that of 1,2-dimethyl-4-ethylbenzene.

#### Calibration factor ( $f_C$ ) and type of aromatic hydrocarbon

An examination of the calibration factor,  $f_C$ , data in Table III disclosed that the molecular structure of the compounds plays an important role in determining the value of this factor, while within each type the variation in value is relatively small. Referring to Table III, for all alkylbenzenes the values are from

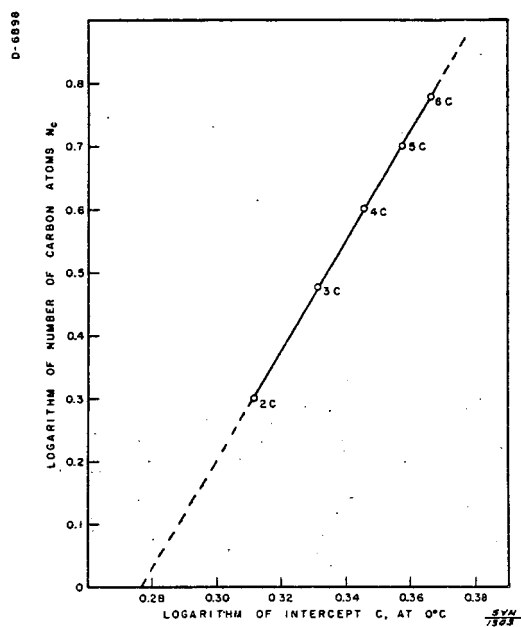


Fig. 3. Correlation between number of carbon atoms in the alkyl group,  $N_c$ , and intercept C at 0°C.

0.93-1.10 with an average of nearly 1.0; for indenenes, styrenes, and naphthalene, 1.15, 1.1, and 1.14; and for indan and tetralin, 1.65 and 2.05. Considering the benzene nucleus as a common structural center for all compounds, the alkylbenzenes are obviously in one group; styrenes, indenenes, and naphthalene, which all have unsaturation in the other part of the molecule, form another group; indan and tetralin, with the non-benzene part being saturated and cyclic, are different from the other two groups. The difference between indan and tetralin is probably due to the number of carbon atoms in the saturated cyclic part of the molecule. It is interesting to note that benzofuran, having an unsaturated part in addition to the benzene nucleus, has a value of 1.15, quite similar to that of the second group although it contains an oxygen atom.

Based on this observation about the  $f_C$  values and structures,  $f_C$  values for some hydrocarbons which were not available in this laboratory were assumed to be equal to those of either their isomers or of structurally similar compounds. Thus,  $f_C$ , 1.09, for 1,3-dimethyl-5-ethylbenzene was used for estimation of all dimethylethyl benzenes; 1.11 for 1-methyl-3,5-diethylbenzene for all methyl-diethyl benzenes; 1.65 of indan for all methyl indans; 1.15 of benzofuran for all methyl benzofurans, and 1.00, an average value for 1,2,4,5- and 1,2,3,5-tetramethylbenzene, for 1,2,3,4-tetramethylbenzene.

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Utilization of Tar from Low-Temperature Carbonization of Coal  
E. W. Lang and J. C. Lacey, Jr.  
Southern Research Institute  
Birmingham, Alabama

Recently-developed processes for fluidized low-temperature carbonization of coal promise to make available a large amount of low-cost tar in the near future. Because of the simplicity and relatively low cost of these processes, the power utility industry is seriously considering low-temperature carbonization as a means of reducing the cost of the solid fuels used. One large steam-generating plant could produce, through low-temperature carbonization of its coal, approximately 50,000,000 gallons of tar per year. The profitable disposition of the tar has been the major obstacle to commercialization of low-temperature carbonization of coal for several decades. The problem in finding outlets for the tar is difficult because it is quite different from coke-oven tar in physical and chemical properties and because the quantity that may be produced by several large steam-generating plants is so large. A fair amount of work has been or is now being carried out on determining the properties and composition of the tar (8, 10) and on developing uses for the tar (1, 2, 3, 4, 5, 6, 7, 9, 13, 14). But very little technical information is available from these programs. In the interests of making more information available, we wish to present the results from a preliminary program carried out in 1955 on the utilization of low-temperature tar.

This paper presents a summary of the work carried out at Southern Research Institute to evaluate the tar produced from Alabama bituminous coal and to investigate, in a preliminary manner, some methods for utilizing the tar. Also presented are the technical and economic aspects of two proposed means of processing the tar to salable products. The program was sponsored by the Alabama Power Company and its affiliate, Southern Services, Inc., in the interest of finding a means of reducing the cost of solid fuels.

Experimental Program on Utilization of Tar

This program on tar utilization was undertaken to provide a sounder basis for evaluating the potential of low-temperature carbonization for the sponsoring power utility. A prior program (11) for this power utility had demonstrated in a pilot plant that agglomerating coals could be carbonized economically in a fluidized-bed process. For a power plant application, the cost for carbonization and non-recoverable heat value of the original coal must be borne by the sale of the tar. Cost estimates indicated that carbonization would be economic if the tar could be sold for \$0.08 to \$0.10 per gallon. Disposal of the tar as a heavy liquid fuel would not always bring this required price. Therefore, for economic disposal of the tar, some premium values of the tar must be realized. Insufficient information was available in the literature on processing of low-temperature tar to marketable products to permit economic evaluation of proposed methods of processing. Also, the applicability of available data to the particular tar produced from

Alabama coals was not known. Therefore, an investigatory program was carried out (1) to evaluate in a preliminary manner various means of utilizing or converting the tar from the Alabama coals, (2) to determine approximate yields of salable products, (3) to reveal avenues of research that might be followed, and (4) to permit an approximate price tag to be put on the tar in terms of processing costs and prices of marketable products. The program was not intended to develop detailed and optimum procedures for each type of processing that was considered. Therefore, the results from this program are not precise, and the operating conditions and yields are probably not the optimum values that further research will provide.

### Tar Composition

Tar from the low-temperature carbonization processes is considerably different from high-temperature coke-oven tar. Low-temperature tar has undergone less thermal cracking and is, therefore, less aromatic in nature. It may be regarded as intermediate in nature between coke-oven tar and crude petroleum. Very few chemical compounds are present in sufficient amounts to permit their economical separation and recovery.

The tar used in this program was produced by carbonizing America Seam coal, a high-volatile bituminous coal from Alabama, at 950° F in a continuous fluidized-bed carbonization pilot plant (11). The tar is quite similar in physical and chemical properties to tars produced in other low-temperature carbonization processes from a variety of coals.

The composition of a typical tar used in these studies is shown in Table I. About 12% of the tar consists of low-boilers distilling below 235° C, 30% is middle oil boiling 235° to 360° C, and 58% is accounted for by the pitch and distillation loss. These yields are similar to those from coke-oven tar. The tar-acid content of the low-temperature tar (about 30% of distillate) is greater than that of high-temperature tar. The neutral oil from the distillate contains roughly 50% aromatic hydrocarbons, 40% saturated hydrocarbons, and 10% olefinic hydrocarbons. Table I also shows the composition of the low boilers (distillate to 235° C), the heavy distillate (boiling 235-360° C), and the distillate tar acids.

The pitch amounts to over 50% of the tar. It has a softening point of about 100° C after the distillables to 360° C have been removed. The pitch contains 4-10% char dust carried through the dust-collection equipment and 11-29% of the pitch is insoluble in benzene. Commercial dust collection equipment will keep the dust content of the pitch from a large plant at a lower level.

### Light Distillate

The light distillate fraction boiling below 235° C has a much greater value than the other fractions because approximately 30% of it consists of phenol, cresols, and cresylic acid. Aromatics (40% of the remaining neutral oil) can be recovered, but the oil would be more valuable if the aromatic content of the oil were increased. Therefore, two runs were made in a continuous bench-scale pressure reactor using reforming conditions to study the possibility of converting the naphthenes in the light distillate to aromatics.

The reactions were carried out in a bench-scale continuous reactor containing 550 ml of 1/8-in. standard molybdena-alumina catalyst. The conditions of the runs included a space velocity of 0.4, a catalyst temperature of 525° C, and a flow of hydrogen at 370 psig.

In two runs made with neutral oils from the light distillate, the aromatics content of the oil was increased from 38% to 65% at a yield of 71 vol-%. Nitrogen and sulfur compounds were practically eliminated under these conditions.

#### Heavy Distillate

To study the possibility of converting the heavy distillate to more valuable low-boiling compounds, the fraction of the tar boiling between 235° C and 360° C, including the tar acids, was treated by catalytic means in both batchwise and continuous runs.

The four batchwise hydrogenation runs were made with maximum hydrogen pressures of 3000 to 4000 psig, temperatures of 450° C to 500° C, and a molybdena-alumina catalyst. After a reaction time of 1.5 hr, the yield of oil was 93 vol-%; 45% of the product boiled below 235° C, and the product contained 55% aromatics. The consumption of hydrogen was 5.5% of the weight of the tar. These runs indicated that 475° C was about the optimum temperature, and that the yields were much lower with longer holding times and at higher temperatures.

The continuous runs were made in a bench-scale unit which had a reactor catalyst volume of 550 ml. They were made at a temperature of 480° C, a hydrogen pressure of 3000 psig, and a space velocity of 0.4 to 0.8. The catalyst was 1/8-in. pellets of molybdena alumina. Under these conditions, very little of the aromatic compounds was hydrogenated and the desired degree of cracking to the low-boiling compounds was accomplished. The tar acids were practically eliminated under these conditions. The results from the continuous runs were quite similar to those from the batchwise runs. On the basis of five runs, the best yields at these conditions were approximately 92 vol-% and the amount of the product boiling below 235° C was 50%. The product contained 40% aromatics.

The hydrocracked oils boiling below 235° C still contained considerable amounts of naphthenes and their conversion to aromatics via reforming was studied in a single continuous run. The equipment and conditions were the same as used for reforming of the low-boilers distilled from the tar. An oil yield of 74 vol-% was obtained. The product contained 80% aromatics as compared to 44% aromatics in the charge stock. A more complete study of reforming of hydrogenated or hydrocracked oils from tar should demonstrate higher yields.

#### Neutral Heavy Distillate

It is probable that in commercial processing of the distillate oils, the tar acids will be extracted for separate processing before the oils are catalytically treated because such treatments destroy the tar acids. A number of continuous runs was made with this neutral heavy distillate to determine the effect of thermal cracking at atmospheric pressure with and without catalyst and the effect of a low-pressure reforming-cracking reaction. The neutral heavy distillate used for these runs was the fraction of the total tar boiling from 235° C to 360° C after the tar

acids were extracted with caustic washing. Under the best conditions, the heavy oil was cracked in a single pass to products of which 40% boiled below 235° C and which had high aromatic contents of 75% to 80% at a yield of 75 vol-%.

Thermal cracking runs on the neutral distillate made without a catalyst at 600° C and at atmospheric pressure resulted in yields of approximately 80 vol-%. Only about 17% of the product boiled below 235° C. Another series of runs was made using molybdenum sulfide-alumina catalyst and hydrogen at atmospheric pressure at a space velocity of 1.0. At a temperature of 640° C, the yield was 55%, and the product contained 77% aromatics and 22% of oils boiling below 235° C. At a lower catalyst temperature of 520° C, the yield was 87%, but the product contained only 16% of oils boiling below 235° C. These runs indicated that satisfactory yields of cracked products can be obtained only when a catalyst and sufficient hydrogen pressures are used to prevent cracking from proceeding too far.

A series of runs on the neutral heavy distillate was then made using hydrocracking-reforming conditions of 500 to 750 psig hydrogen pressure and temperatures of 480 to 550° C. The previous runs with total heavy distillate showed that fair yields of aromatics boiling below 235° C could be obtained by first hydrocracking the oils to low-boiling oils and then reforming the low-boilers to aromatics. This present series was made under conditions that combined those of the previous two-step treatment. A fairly high temperature was selected to give sufficient cracking and dehydrogenation and a moderate hydrogen pressure was selected to prevent over-cracking of the compounds so that good liquid yields would be obtained. The selection of these conditions was based partially upon a series of batch reactions with heavy distillate.

With the use of a molybdena-alumina catalyst at about 480° C, a hydrogen pressure of 750 psig, and a space velocity of 1.0, yields were 75-91 vol-%. The product contained 73-80% aromatics and 40% boiled below 235° C. With a temperature of 550° C, hydrogen pressure of 500 psig, and a space velocity of 0.4, the yield was 74 vol-%, the product contained 79% aromatics, and 46% of the product boiled below 235° C. In a commercial operation, the oils boiling above 235° C would probably be recycled to the reaction so that only low-boilers would be produced. One run was made to determine the effect of recycling the high-boiling oil. The yield of product was 66 vol-%. The product contained 93% aromatics and 26% boiled below 235° C.

The combined reformate boiling below 235° C from the primary run and the recycle runs was carefully fractionated and the aromatics in each fraction determined. This analysis indicated that the combined chemical oil contained 4% benzene, 8% toluene, 10% xylenes, 16% naphthalene, 30% substituted benzenes, and 32% saturated hydrocarbons.

#### Tar Acids

As shown by the typical analysis in Table I, approximately 40% of the tar acids from the total distillate consists of phenol, cresols, and xylenols. About 60% consists of high-boiling, highly-substituted alkyl phenols for which there is little demand at the present. The research program has shown that the tar-acid fraction boiling from 170 to 235° C (including xylenols) will form hard thermosetting resins with formaldehyde. The removal of small amounts of impurities

from individual tar acids appears to be a major problem.

One means of utilizing the tar acids is to convert the higher-boiling ones which have little value to the simpler, more valuable low-boiling phenolics. The hydrocracking of these high-boiling tar acids was studied in five batchwise runs with a molybdena-alumina catalyst in the presence of water. Tar acids boiling from 235 to 360° C were hydrocracked at a temperature of 420° C, in the presence of 10% addition of water, and a hydrogen pressure of 2600 psig. The yield was 92 vol-%. The product contained 82% tar acids and 23% oils boiling below 235° C. The tar acids boiling in the intermediate range of 235 to 300° C were hydrocracked at 460° C and 2100 psig hydrogen pressure to give a yield of 90 vol-%. The product contained 50% tar acids and 53% boiled below 235° C. Hydrocracking of the heavy tar acids boiling at 300-360° C resulted in a yield of 84 vol-%. The product contained 50% tar acids, and only 23% of the product boiled below 235° C. Additional runs with this fraction were made in which nitrogen replaced some of the hydrogen in an attempt to limit the hydrogenation of the hydroxyl groups and yet provide sufficient pressure to suppress the cracking to gases. These runs gave rather low yields of oils and a large amount of coking.

#### Pitch

Approximately one half of the tar consists of hard pitch. Therefore, no plan for conversion of the tar will be successful unless attractive markets or methods of conversion for the pitch are found. The pitch might be sold in the large-volume markets of road asphalt or pitch, roofing pitch, electrode binder pitch, or for a premium fuel in open-hearth furnaces of steel mills. The pitch might also be converted to pitch coke or hydrogenated to give more of the low-boiling chemical oil. Preliminary investigations were made for adapting the pitch to these various outlets. Additional work on making the pitch more stable to weather is needed if it is considered for uses such as road and roofing pitch.

Experiments showed that the specifications for highway road-tar primer could be met by blending high-boiling neutral oil with pitch. However, this method would use up more of the heavy distillate than pitch and would degrade the value of the distillate used to road-tar price.

Electrode binder pitch must contain at least 20% of so-called "beta resin" which is that portion soluble in quinoline, but insoluble in benzene. Normally, low-temperature tar pitch has a very small amount of this beta resin. A series of experiments demonstrated that the beta-resin content of the pitch could be increased to the range of 30 to 50% in yields greater than 95% by air-blowing at 250° C. No catalyst was used in any of the runs. This air-blown pitch meets most specifications for electrode binder pitch, but its utility for this purpose needs to be tested.

Coking of the pitch was studied in five batchwise retort runs made at 700° C. The average yield of coke was 51% and that of tar was 31%, with the remainder being water and gas. The coke had a volatile content of 5%. The pitch used for these tests had a high content of char dust which caused a high ash content in the coke. The tar from the coking of pitch was very viscous and contained only 19% of oils distillable to 360° C.

## Tar Hydrogenation

A limited number of batch hydrogenations was carried out using the total tar which had been topped to 235° C. Such hydrogenation of the total heavy tar might be considered for commercial utilization of the tar if previously mentioned uses of the tar do not provide sufficiently attractive outlets. Low-temperature tar is much more reactive than coke-oven tar, and has been hydrogenated to low-boilers in yields of approximately 100 vol-% in other research programs. The two runs made in the present program were carried out at temperatures of 450 and 470° C, and at maximum hydrogen pressures of about 3000 psig. Yields of 90 and 98 vol-% were obtained, and 20 to 30% of the product boiled below 235° C. The conversion to low boilers was not as great as desired, and further study is needed.

## Possible Methods for Processing the Tar to Marketable Products

A large number of means for utilizing the tar are potentially available—from crude uses such as for fuel and road tars to complete conversion to low-boiling aromatics. The optimum combination of processing methods will be determined through future research, by existing and future markets, and by the economics of such combinations of processing methods.

Several schemes for partial or total conversion of the tar to marketable products were considered on the basis of the results from the preliminary experimental program and on published data. Two possible methods of processing the tar are presented to illustrate what might be done, and to indicate the approximate economic potentials of such processing plans. The estimates were based on a plant processing 41,600,000 gallons of tar per year produced by fluidized carbonization of 6,000 tons of America Seam coal per day. The costs of equipment and processing were obtained from published data on plants carrying out these or similar steps. Since the cost data used were averages of as many as 20 to 30 reported costs, it is believed the data are representative of the cost of an average processing step. In each case, conservative (higher-cost) figures were used. The tar was charged to the tar processing plant at \$0.086/gal because a cost study indicated that such a price would give a net return of 10% after income taxes on a carbonization plant located in Alabama. These costs were based, in part, on an engineering cost study of fluidized carbonization by United Engineers and Constructors, Inc. (12).

The first of the two proposed plans for tar processing involved using a portion of the tar without chemical conversion and converting the remainder by hydrocracking. The low-boiling oils are removed and refined to tar acids and a neutral oil. The pitch and nonaromatics from the heavy distillate are sold as road binder. The aromatic portion of the heavy distillate is hydrocracked to low-boiling oils. The refined products consist of low-boiling aromatics, cresylic acid, and gasoline blending stock.

The total plant cost was estimated to be \$6,470,000, of which \$2,628,000 was for the hydrocracking unit. After including \$1,310,000 for working capital, the total capital requirements were \$7,780,000. The processing costs included amortization, direct and indirect production costs, raw material (tar) costs, and sales and administrative costs. The estimated net income after income taxes was

\$979,000, which gives a net yearly return on the investment of 12.6%, or a payout time of 4 years.

The second plan was for the complete conversion to low-boiling products. This plan was proposed for the eventuality that the pitch and heavy distillate cannot be sold in existing markets or would bring only fuel prices.

This method of utilization calls for removing the tar acids boiling below 300° C, and hydrocracking the rest of the tar to oils boiling below 235° C. The heavy tar acids are also hydrocracked to cresylic-acid range or below. The final products consist of refined tar acids, refined aromatics, and a gasoline blending stock. The over-all yield of finished products was 68 gallons per 100 gallons of crude tar.

The estimated cost of the plant was \$13,152,000, including working capital. The total yearly costs for processing the tar were estimated at \$3,733,000. The net income after income taxes for this plan is \$912,000, which provides a return on the investment of 6.9%.

#### Present Outlook

The return on the investment for either of these plans is lower than that expected by most chemical companies for processes that will involve heavy expenses for development work. There are several factors that may improve the economics of processing low-temperature tar: (1) further research may result in higher yields of the valuable products from the tar; (2) further research and advancing technology are expected to reduce the complexity and the costs of processing the tar; (3) long-term increases in costs of competitive raw materials and of finished products will better the economics of tar processing; (4) further development work on the carbonization process should result in increased yields of tar from the coal and lower costs of carbonization.

Counterbalancing these optimistic factors are some dampening factors that have become apparent since the fall of 1957. The general recession in 1958 caused softening of prices of the aromatic chemicals and of certain fuel fractions for which some of the tar would be used. It may be several years before these losses may be overcome by rising prices. The increasingly large amount of imported petroleum of the past few years has softened the price of fuels and petroleum products with which some of the tar products must compete.

It now appears that the conversion of tar into chemical products on a commercial scale is a matter of 5 to 10 years in the future. When petroleum and residual fuel prices increase to approximately \$0.10/gal at inland coal-producing areas, operation of commercial carbonization plants should be profitable through the sale of tar as a liquid fuel. Once low-temperature carbonization is on its feet through sale of tar as fuel, then commercial processing of the tar to chemicals and higher-priced products will follow.

Table I. Properties of Typical Tar from America Seam Coal

Specific gravity 25/25° C, 1.10

Distillation yields, weight % (Hempel)

to 170° C	1.4
170-200	3.3
200-235	7.6
235-270	7.3
270-300	7.5
300-360	14.3
pitch	51.8
loss	6.8

Composition of distillate, volume %

tar acids	28.5
tar bases	2.9
neutral oil	68.6

Composition of distillate tar acids

<u>Fraction</u>	<u>Major Component</u>	<u>Weight %</u>
170-200° C	phenol	3.1
200-210	cresols	13.9
210-235	xlenols	22.0
235-300		20.8
above 300 and loss		40.2

Composition of distillate neutral oil, volume %

Olefins	8.1%
Aromatics	47.3
Saturated hydrocarbons	44.6

Composition of low boilers (to 235° C), volume %

Tar acids	28.5
Tar bases	2.2
Neutral oils	69.3
Olefins	11.2
Aromatics	33.2
Saturated hydrocarbons	50.6
Naphthenes	41
Paraffins	59

Composition of heavy distillate (235-360° C)

<u>Distillation range</u>	<u>Weight %</u>
to 235° C	6
235-270	14
270-360	48
Residue	32

Composition, - volume %

Tar acids	35.7
Tar bases	3.4
Neutral oil	61.0
Aromatics	51.6
Olefins	19.2
Sat'd hydrocarbons	29.2

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STUDIES ON LOW-TEMPERATURE LIGNITE TAR  
I. GENERAL TAR CHARACTERISTICS AND PROCESSING

by

H. R. Batchelder, R. B. Filbert, Jr., and W. H. Mink  
Battelle Memorial Institute  
Columbus, Ohio

BACKGROUND AND HISTORY

A process for the low-temperature carbonization of Texas lignite in dilute suspension was developed by the U. S. Bureau of Mines at Denver, Colorado, in cooperation with the Texas Power & Light Company as part of a program for the more efficient use of this material. Work at Denver was carried through the pilot-plant stage. Promise of this process was such that the Aluminum Company of America installed a prototype carbonizer in combination with the power plant for their aluminum smelting installation at Rockdale, Texas. The boilers for the power plant were designed primarily to handle dried Sandow lignite, but were further designed so that lignite char would be acceptable as an alternate fuel. This permitted the production of the desired amount of tar without regard to the amount of solid fuel required for the boilers. The plant is 360,000-kw capacity, serviced by three boilers, in turn supplied by nine lignite driers. The prototype carbonizer was sized to handle the output of one drier only, with provision for transport of the hot char to the fuel bunkers. In effect, the carbonizer was on a bypass to the main line between the drier and the boiler. If all of the lignite were carbonized, tar production would be of the order of 50 million gallons per year.

The lignite is strip mined and transported by conveyor belt to the driers or field storage. Each drier has a capacity of 50 tons per hour and normally dries the lignite to 2 to 4 per cent moisture. The crushed dried lignite is picked up by recycle carbonizing gas, together with some air admixture, and is carried into the retort. Part or all of the necessary heat may be provided by combustion of tar vapors with process air within the retort. An external furnace is provided to supply what additional heat may be required. After the char is separated, the tar vapors are

condensed and the condensed water decanted. A good review of the carbonization work is given in the Bureau of Mines papers published by Parry et al.\*

In 1954, Battelle was asked by Texas Power & Light and Alcoa to undertake studies leading to the exploitation of this tar. The work that will be reported here will cover the processing of this tar, the characterization studies, analysis of products, and the type of reactions of the tar components. No discussion of the utilization of this material is included.

#### GENERAL PHILOSOPHY OF APPROACH

The information available on low-temperature tars from lignite at this stage was quite sparse and, in many cases, self-contradictory. It was known, however, that the tar was an extremely complex mixture of a variety of hydrocarbon types, as well as compounds of oxygen, nitrogen, and sulfur. Throughout the course of this work, the general philosophy has been that attempts would be made to find uses for the crudest possible fractions, and that subsequent separations and refinements would be undertaken only when the work to that point had shown that further refinement was essential to any attractive utilization.

#### GENERAL CHARACTER OF THE TAR

The tar produced at Rockdale can be classed as a truly "primary" or virgin tar. The operating temperature of the carbonizer is relatively low. The rate of heating of the lignite and evolution of the volatile matter is rapid, and the vapor residence time of the liberated material is very short. None of the conditions obtain which in a by-product coke oven allow for extensive cracking and rearrangement of the components of the volatile matter. Consequently, the tar character reflects closely the character of the lignite charge.

It is this circumstance which probably contributes most to the complexity of the tar composition. Where extensive thermal reactions are possible as in the coke oven, most of the more unstable compounds are converted to a relatively few simple, highly stable configurations. A substantial part of the nitrogen and sulfur is liberated as ammonia and hydrogen sulfide, and appreciable quantities of hydrogen and methane are formed by the pyrolysis of hydrocarbons.

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\*Parry, V. F., Landers, W. S., Wagner, E. O., Goodman, J. R., and Lammers, G. D., "Drying and Carbonizing Fine Coal in Entrained and Fluidized State", Bureau of Mines Report of Investigations 4954, 1953.

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In the lignite tar, where these degradative reactions are at a minimum, a large proportion of the originally evolved compounds probably survive unchanged. Thus, throughout the whole boiling range of the distillates we find paraffinic, naphthenic, olefinic, and aromatic hydrocarbons, with oxygen, nitrogen, and sulfur substitution, and probably the undistilled material was of the same general nature.

#### EARLY DISTILLATION WORK

In the first approach to this problem, distillation was selected without question as the first means of separating crude fractions from the lignite tar. Because of many references to the instability of this material, particularly at higher temperatures, we used continuous distillation under vacuum with the minimum practical heating time. A series of these experiments showed an expected relationship between the volume of distillate recovered and the softening and/or viscosity of the residues. Comparison of the distillates recovered at various distillation temperatures soon showed that the composition did not vary particularly with the boiling point. In other words, the same classes of compounds were present in a distillate that represented 20 per cent of the primary tar as in a distillate that represented 50 per cent. As we went further with the study of these oils, separation into fractions of various boiling ranges supported this observation very strongly. The evidence was abundant enough to indicate that this constancy of composition extended throughout the tar, and that the undistillable residues were of the same general composition as the light distillates. The properties of the primary tar itself are shown in Table 1, and average composition of the distillate in Table 2.

TABLE 2. AVERAGE COMPOSITION OF LIGNITE TAR DISTILLATE

Compound	Volume Per Cent
Tar Acids	26
Tar Bases	4
Neutral Oils	70

#### SOLVENT EXTRACTION OF PRIMARY TAR

In studying the products obtained by this distillation of the primary tar, in many cases we found that the heavier portions of the tar had characteristics which were not particularly desirable. However, it was impractical to treat these fractions for the removal of the offending classes of compounds. For example, we had found quite early that a caustic soda treatment of a high-boiling distillate fraction for removal of tar acids was not promising because of emulsion formation and the difficulty of the separations. On this basis, the application of separation means to the primary tar itself appeared to be in order.

TABLE 1.  
PROPERTIES OF PRIMARY LIGNITE TAR

Ash, per cent	0.4				
C-I, per cent	1.3-1.6				
Water, per cent	3-4				
Specific Gravity, 25/25 C	0.9867				
Viscosity, cp, 28 C	820				
Elemental Composition, per cent water-free basis	<u>C</u> 81.0	<u>H</u> 8.7	<u>N</u> 0.7	<u>S</u> 0.7	<u>O(diff)</u> 8.5
Distillation, ASTM D20-52, weight per cent (dry basis)					
To 170 C	2.5				
170-235 C	16.4				
235-270 C	11.6				
270-300 C	12.6				
300-Decomposition Temperature	31.0				
Residue at Decomposition Temperature	21.0				
Loss	4.9				
Residue at 300 C	52.0				
Decomposition Temperature, C	337				

#### Batch Shake-Out Experiments

Because of our earlier work on distillation and the work of others on the separation of tar acids, we were led to explore the solvent extraction of the primary tar and tried first a two-solvent system comprising aqueous methanol\* and hexane.

It seemed reasonable to expect that, by this means, a residue could be produced from the hexane-soluble fraction which would contain little or no polar materials. At the same time, the high-boiling tar acids and polar materials normally in the residue from the distillation should now be found in, and be recoverable from, the methanol extract. In a series of batch shake-outs, we found that separation could be achieved, and made a start toward defining the preferred conditions for the separation. A series of single batch shake-outs was made to determine the desired temperature of operation, the results of which are shown in Figure 1. As the temperature was increased from 66 to 120 F, it was found that the extent to which insoluble material was dispersed through the methanol phase decreased steadily until, at 120 F, the insoluble material was cleanly separated and was fluid enough so that it could be withdrawn without difficulty. Also, at this temperature, the material loss in the course of the experiment and the yield of insoluble material were markedly less than in the experiments conducted at lower temperatures. Temperatures much beyond 120 F would have required either the substitution of a higher boiling solvent for hexane or the conducting of experiments at higher than atmospheric pressure. Neither seemed desirable at this stage, since there was no reason to anticipate unsatisfactory operation at 120 F.

Another series of single batch shake-outs was made to study the effect of varying the solvent ratio on the products obtained. Increasing either solvent decreased the amount of insoluble material. Increasing the methanol ratio at a constant hexane ratio increased the yield of methanol solubles. The concentration of caustic solubles in the methanol solubles was also increased by increasing the methanol ratio up to a ratio of about 2. Higher ratios, however, resulted in a gradual reduction of the concentration of caustic solubles.

It can be shown that the total recovery of caustic solubles from the primary tar increases with increasing methanol ratio. In the process of recovering more tar acids by using higher methanol ratios, there is included more and more non-tar-acid material in the methanol solution. For maximum purity of recovered materials, low methanol ratios would be used; for maximum removal, high ratios would be used. Practically, the maximum removal in usable purity is the goal.

Because the process is essentially a partition of the tar acid material between the methanol and the hexane, the effect of increasing

\* Whenever methanol is used here, it refers to a methanol-water solution, usually 70 weight per cent methanol.

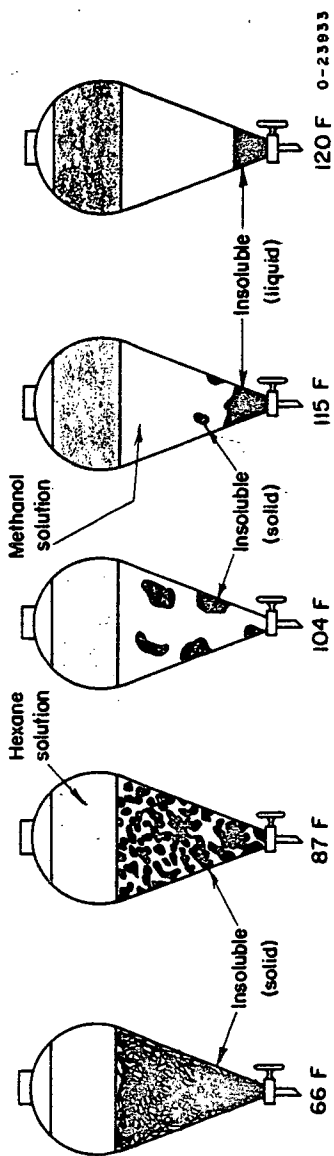


FIGURE 1. EFFECT OF TEMPERATURE ON SOLUBILITY OF TAR IN SINGLE BATCH SHAKE-OUT SOLVENT EXTRACTION

hexane ratio is substantially that achieved by decreasing the methanol ratio, except that the yield of insoluble material is decreased by an increase in either solvent. These preliminary experiments formed the basis for initial operation of the continuous unit.

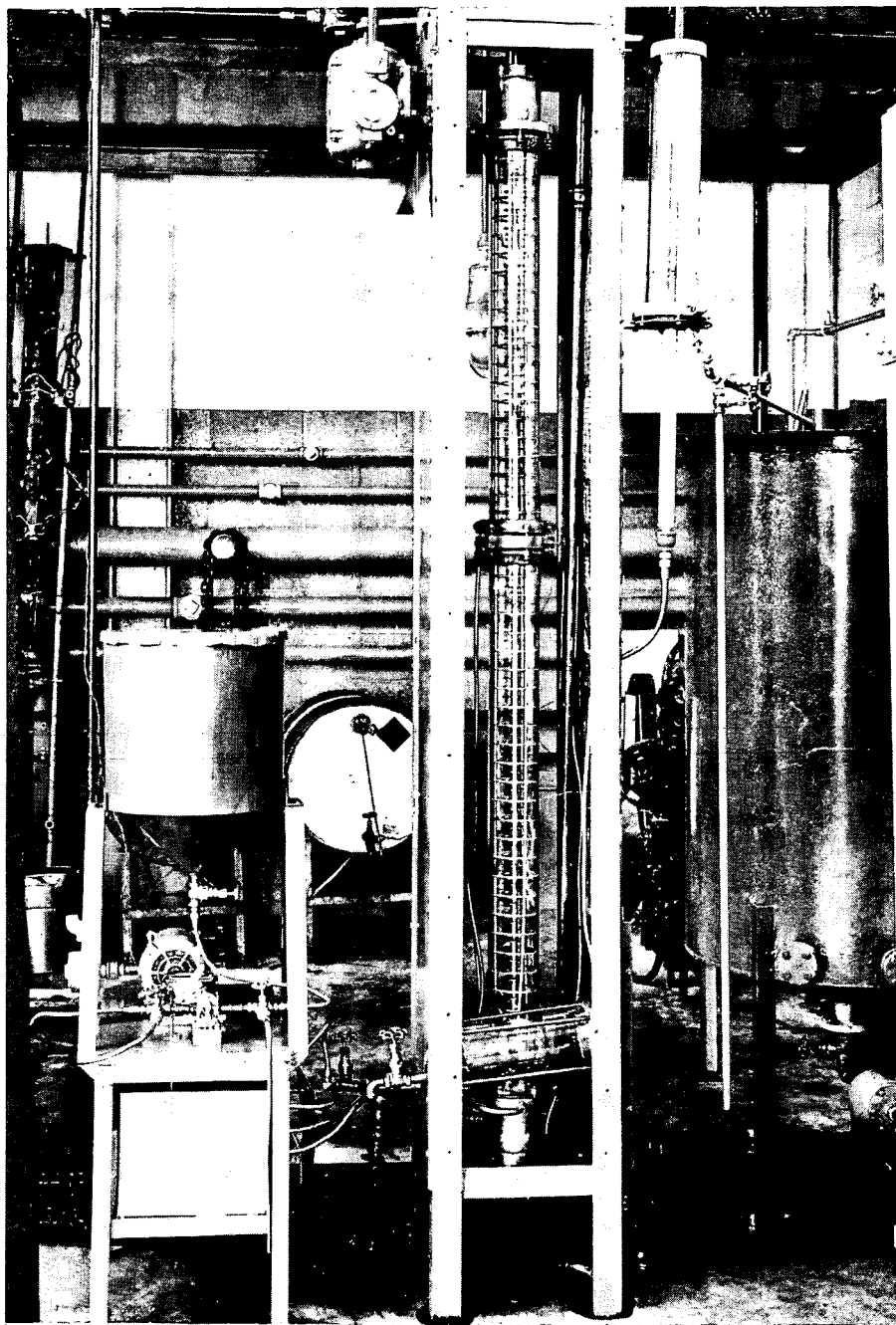
### Operation of Rotating Disc Contactor Unit

#### Description of RDC Unit

The RDC column proper (shown in Figures 2 and 3) is constructed of two 4-inch flanged glass-pipe sections. The top section is 3 feet long and the bottom section is 4 feet long. The stator rings shown in Figure 3 are 3-13/16 inches in OD and 2-3/8 inches in ID. Teflon gaskets are sandwiched between the 20-gage stator rings to seal the ring to the side of the glass pipe. This method of construction was used because the inside diameter of the glass pipe used varies by as much as 1/8 inch. Three holes are punched in the stator rings and gaskets, and 1/4-inch rods inserted through the holes to hold the rings and gaskets. The compartments are formed by using spacers of 1-3/4-inch lengths of 3/8-inch tubing. The rotors are 20 gage and 2-1/8 inches in diameter, and are soft soldered to a 5/8-inch shaft.

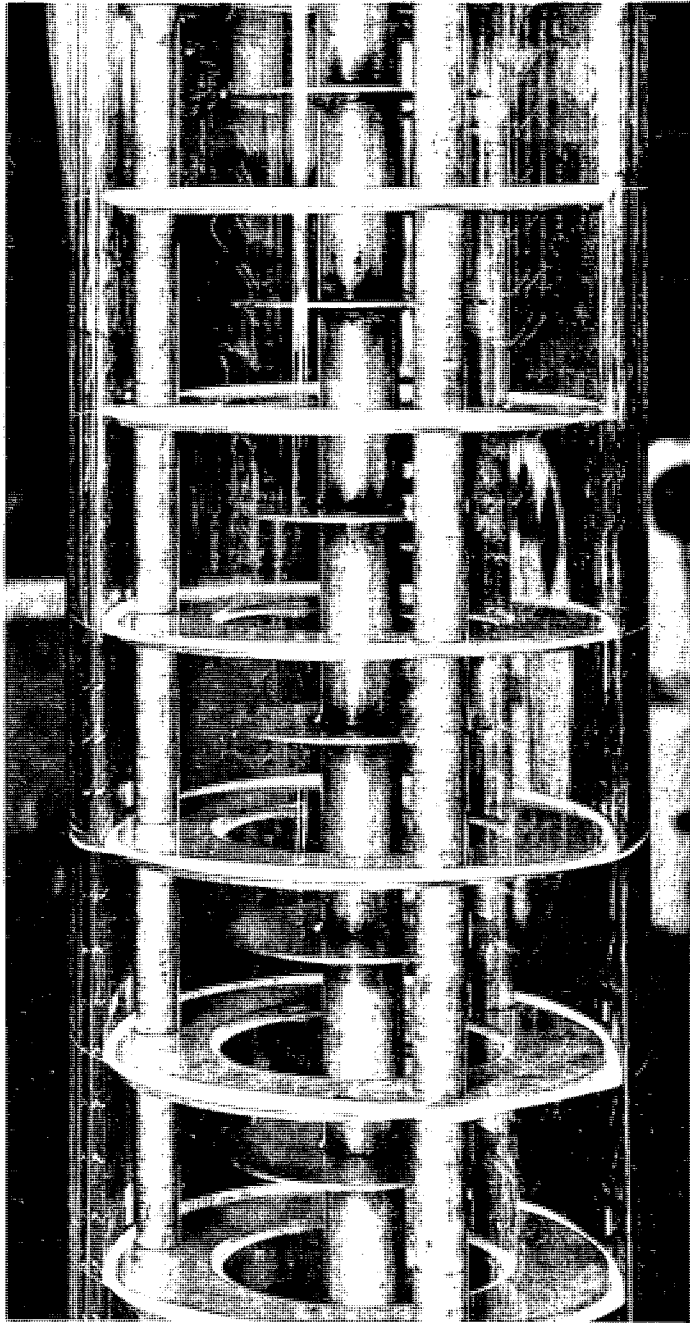
The two glass units are joined together in the center by means of a 1-inch-thick ring. The ring (Figure 2) is drilled and tapped so as to provide an entry for tar feed, a bearing support for the rotor shaft, and a passageway for fluids in the column. The fittings at the ends of the column are similar in construction to the center piece, except that an extension, consisting of a section of 4-inch tubing, forms a settling zone. The extract is removed through a 3/4-inch pipe and fed to a second settling chamber. Extract is taken off the high end of the settling chamber and fed to a variable-height syphon breaker and from there to a storage tank. The variable-height syphon breaker permits balancing the levels of solvent in the column. Tar is fed to the column by means of a small calibrated gear pump operated through a variable-speed drive. Solvents are fed to the column from constant-head feed tanks through rotometers. Both solvents and tar are heated in a hot-water bath prior to entry into the column.

The column is supported in an angle-iron framework which is enclosed on all four sides. The top of the framework is connected to a hood which removes vapors from the column and, at the same time, heats the column by drawing air in through a heat exchanger on the side near the bottom. Raffinate from the column is fed to the solvent-stripping unit, a 100-gallon agitated steam-jacketed vessel. An unlagged 4-foot length of 4-inch pipe filled with Berl saddles provides sufficient rectification to strip solvents from the products. After the raffinate has been stripped, the unit is used to strip the extract. In actual practice, after stripping, the methanol solubles contain 25 to 50 per cent water. This is removed by decanting.



N33341

FIGURE 2. RDC EXTRACTION UNIT



N33343

FIGURE 3. ROTATING-DISK CONTACTOR

### Physical Operability of RDC Unit

The first runs in the pilot-plant unit were made to explore the variables which should affect the physical operation of the extraction column, in order that optimum conditions might be used as standard in the subsequent runs. These variables were: rotor speed, feed rate, density difference between phases, and time required for the column to reach equilibrium. Temperature was not considered as an operating variable in the RDC experiments, since an optimum temperature for operation had been established at 120 F through batch shake-out tests as described above. All RDC runs were made at this temperature.

In one run (1:4:4 ratio) feed rates were increased until flooding occurred at a tar feed rate of 2.6 gallons per hour. This corresponds to a total column feed of 350 gallons per hour per square foot of column cross-sectional area. In subsequent runs, the combined flow rate was limited to a maximum of about 270 gallons per hour per square foot.

As the rotor speed was increased from 180 to 215 rpm, the amount of caustic solubles in the methanol solubles increased; but, when the speed was increased further to 270 rpm, an emulsion was formed in the column which made phase separation impossible. All subsequent runs were made at 215 rpm.

Enough difference must be maintained between the density of the raffinate and extract so that the phases may be separated. As each solvent dissolves components of the tar, the density of each solution increases; therefore, the density and density difference will depend not only on the solvents used, but also on the solvent ratios as well. As more water is added to the methanol solution, its density increases so that, for each methanol-water concentration, there is a solvent ratio below which the column will not be operable. These findings are summarized in Figure 4.

For any given methanol concentration, operations to the left of the proper curve will not be feasible because of insufficient difference in density between the two phases. Thus, with 70 per cent methanol, a 1:3:3 ratio is satisfactory, but a 1:5:3 or a 1:1:2 ratio is not. It can be seen from these curves that, for any methanol concentration, there is a hexane ratio above which the column may be operated regardless of the methanol ratio. These curves are not sharp and precise boundaries, but rather the areas of approach to inoperable conditions. These data proved very useful in the selection of solvent ratios for subsequent runs.

### Effect of Operating Variables on Products

As with single batch shake-outs, solvent ratios and methanol concentrations can be selected within operable limits for use with the RDC unit so as to produce products of varying quality and in varying yield. For example, the purity and yield (inversely related) of tar acids in the

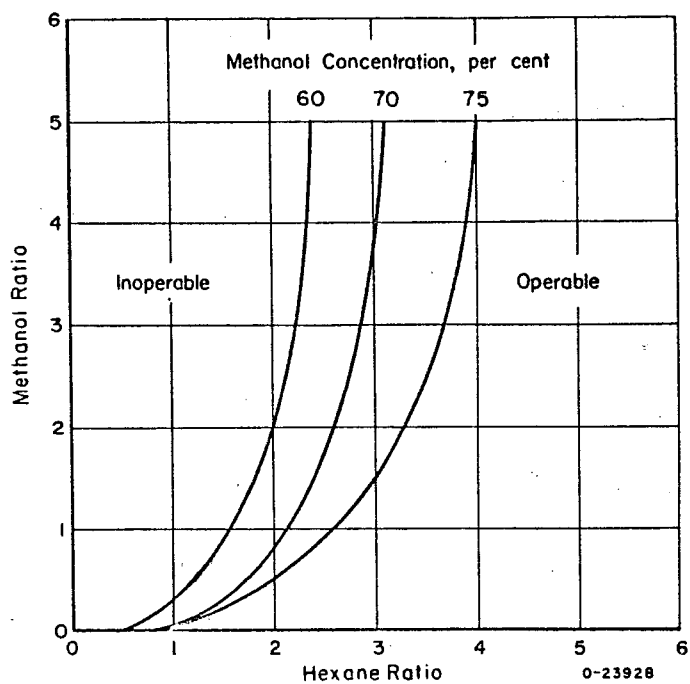


FIGURE 4. LIMITS OF OPERATION OF SOLVENT-EXTRACTION UNIT DUE TO DENSITY DIFFERENCE

methanol extract can be regulated partly by adjusting the methanol concentration. Likewise, the degree of extraction of polar compounds from the hexane-soluble fraction can be adjusted in part by changing the ratios of the hexane-methanol-primary tar streams. The effects of changing these two variables have been investigated within certain ranges in the pilot-plant RDC unit.

The effect of such changes can be followed by determining the fraction of the caustic solubles, originally in the primary tar, which is extracted by the methanol. The total caustic solubles in the tar cannot be obtained directly. However, a number of distillates of various yields were successfully caustic washed and were found to contain about 27 per cent of caustic solubles irrespective of yield or boiling range of distillate. For this reason, the value of 27 per cent was assumed to hold for the primary tar itself.

If the methanol concentration is low, it would be expected that little of the tar would be soluble in it. If, on the other hand, the methanol concentration is high, one would expect that the solubility of the tar, and hence the degree of extraction, would increase. This effect is shown in Figure 5. The position of the curve at 75 per cent methanol indicates that the assumed value of 27 per cent of caustic solubles in the primary tar might be low. If the value of 27 per cent were incorrect, it would have the effect of shifting the curve upward or downward, depending on whether the true value was lower or higher than 27 per cent. It was found in the single batch shake-outs that, whenever the extraction of caustic solubles increased, the concentration of caustic solubles in the methanol solubles decreased. A similar effect for the pilot-plant unit is shown in Figure 6.

The insoluble matter decreased with increasing solvent ratio as in the single batch shake-out tests. However, the column appeared to be more efficient in this separation. At a 1:8:8 ratio, a single batch shake-out resulted in about 4.5 per cent of insolubles while the RDC yielded about 2 per cent. Since Rockdale Run 53 primary tar contained 0.35 per cent of ash, and if it is assumed that char contains 20 per cent of ash, it can be calculated that there was about 1.75 per cent of char in Run 53 primary tar. The curve of Figure 7 appears to approach this value at high solvent ratios.

Figure 8 is a convenient method of showing the effect of solvent ratios for a given methanol concentration. The inoperable zone is defined and the per cent of total caustic solubles extracted is indicated. Because of the few data available, it is not possible to define the shape of the curves showing a constant per cent of caustic solubles extracted as a function of solvent ratios. However, the curve for 70 per cent extraction appears to be approximated by a straight line. The per cent of caustic solubles extracted appears to approach some value around 100 per cent

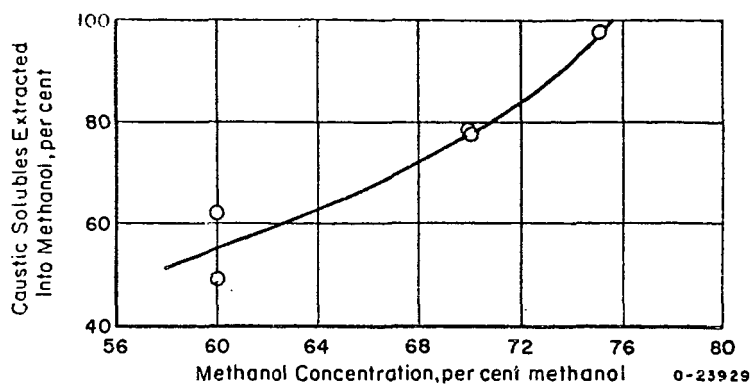


FIGURE 5. YIELD OF CAUSTIC SOLUBLES USING A 1:4:4 SOLVENT RATIO

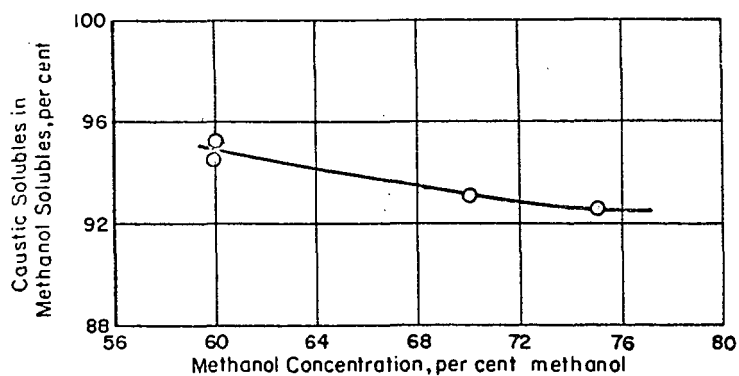


FIGURE 6. CAUSTIC SOLUBILITY OF METHANOL SOLUBLES USING A 1:4:4 SOLVENT RATIO

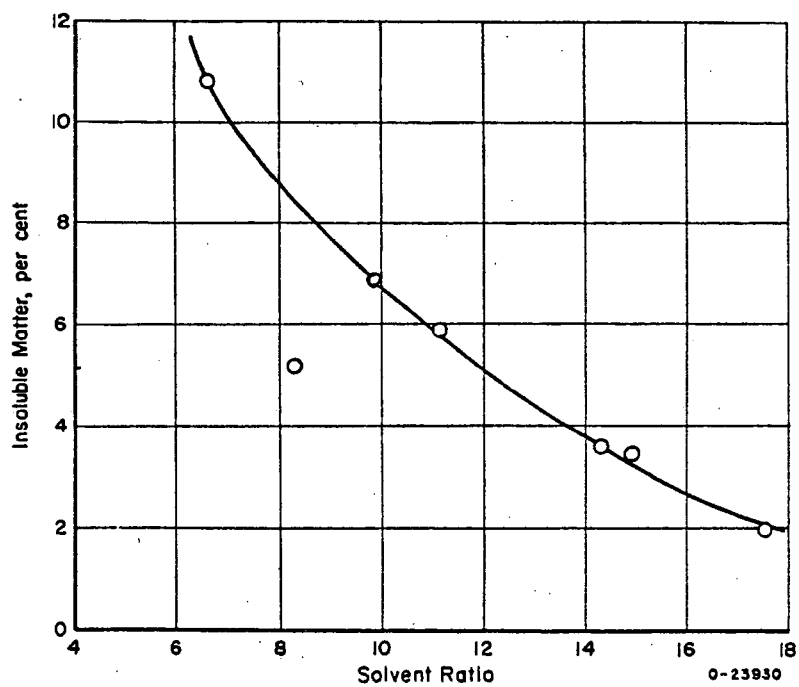


FIGURE 7. INSOLUBLE MATTER AS A FUNCTION OF TOTAL SOLVENT RATIO USING 70 PER CENT METHANOL

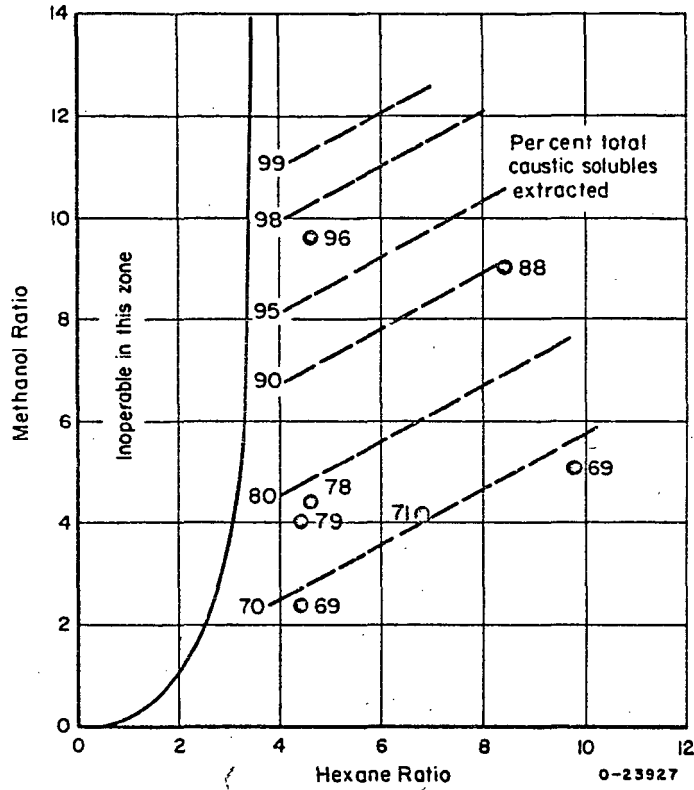


FIGURE 8. PER CENT TOTAL CAUSTIC SOLUBLES EXTRACTED AT VARIOUS SOLVENT RATIOS USING 70 PER CENT METHANOL

asymptotically as the methanol ratio is increased. From the slope of these curves, it is apparent that the methanol ratio has a greater effect on per cent of total caustic solubles extracted than does the hexane ratio under the conditions used.

The relative solubilities of the primary tar in the hexane and methanol phases were determined for 70 per cent methanol at different solvent ratios. These results are shown in Figure 9.

In previous work with the rotating disc contactor, tar feed was introduced at approximately the center of the column. Previous work on solvent-extraction columns has shown that the location of the feed point might have a significant effect on the operation of the column so far as yield and product quality are concerned. For this reason, the rotating disc contactor was altered to permit introduction of tar feed at two locations in addition to the center feed point. The points selected were approximately one-fourth of the distance down from the top of the column and one-fourth of the distance up from the bottom of the column.\* Four runs were made in which the feed point was successively changed from center, to top, to bottom, and finally back to center position. There was no significant change in the column variables other than feed-point location. As a result of this investigation, it was found that the total material extracted from the tar by the methanol varied as follows:

<u>Feed Position</u>	<u>Per Cent Extracted</u>
Center	25.6
Top	23.7
Bottom	23.4
Center	25.9

The relatively small change in the percentage extracted as affected by the feed-point location indicates that the column used probably has considerably more stages than are necessary to perform the desired extraction. In future work, however, the present column will be used, with feed introduced at the center position.

#### Analytical Methods

A 500-ml sample of raffinate is weighed and about 250 ml placed in a tared 500-ml flask. The flask is fitted with a 12-inch Vigreux column and a thermometer extending to within 1/4 inch of the bottom of

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\* In the original design of the rotating disc contactor there were 44 stages, with the feed point being at Stage 20, numbering down from the top. Two other feed points were subsequently provided: (1) "Top", Stage 10, and (2) "Bottom", Stage 32.

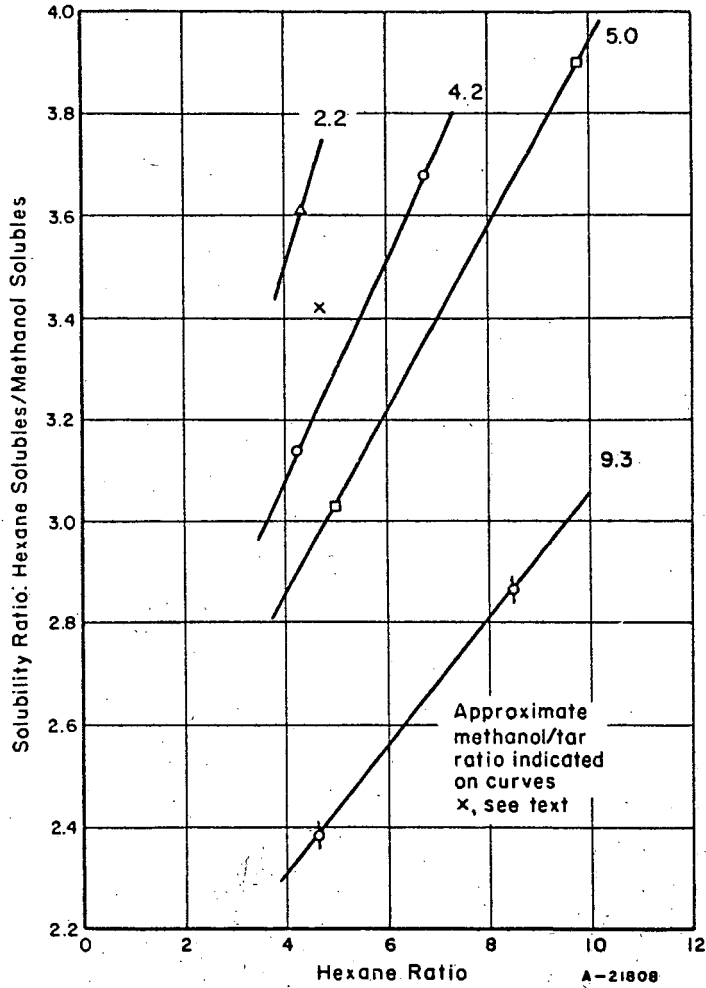


FIGURE 9. RELATIVE SOLUBILITIES AS A FUNCTION OF SOLVENT RATIOS FOR 70 PER CENT METHANOL

the flask. The top of the Vigreux column is fitted with a side arm connecting to a condenser, and a separatory funnel through which is added the remainder of the raffinate sample during distillation.

The flask is heated with a heating mantle, and the hexane distilled over is discarded. When all the raffinate has been charged to the flask the distillation is continued until the pot temperature reaches 210 C. The flask is then cooled and weighed to determine the weight of hexane-soluble residue.

The extract is handled in the same way as the raffinate except that, after all extract has been added to the flask, distillation is stopped when the pot temperature reaches 95 C. The flask is allowed to cool and 200 ml of benzene is added. The contents of the flask are then transferred to a 500-ml separatory funnel, shaken, and allowed to settle. The water layer is drawn off and discarded and the benzene layer returned to the flask. The separatory funnel is rinsed with methyl alcohol, which is added to the contents of the flask. Distillation is continued until the pot temperature reaches 210 C. The flask is allowed to cool and then is weighed to determine the methanol solubles.

The methanol solubles obtained as indicated in the previous section are washed into a 500-ml separatory funnel with three portions of warm 20 per cent sodium hydroxide solution. The solution is allowed to cool to room temperature and 50 ml of ether added. The mixture is shaken carefully and allowed to settle. The ether layer is transferred to a tared 100-ml flask and heated on a steam bath. After the contents have stopped boiling, a vacuum (using a water aspirator) is drawn until no more boiling occurs. The flask is cooled and weighed to determine the non-caustic-soluble material in the methanol solubles. The per cent of caustic solubles is calculated by difference.

A known quantity of the insoluble phase is charged to a tared flask and heated on a steam bath under vacuum to strip it of solvent. The flask is cooled and weighed to determine the insoluble matter.

#### SECONDARY PROCESSING OF SOLVENT EXTRACTION PRODUCTS

For the purpose of providing samples for the characterization and utilization studies, hexane solubles were distilled to yield fores, middle oil, and pitch of various softening points. Both batch and continuous methods of distillation were used. Methanol solubles were usually distilled to an arbitrary cut point of 235 C for the same purpose.

#### ROCKDALE PILOT PLANT

A solvent-extraction pilot plant has been constructed at Rockdale, primarily to provide materials for utilization study on a larger scale. This unit is designed to process about 1000 gallons of primary tar per stream day and to produce five main products. A simplified flow diagram is shown in Figure 10. Tar, aqueous methanol, and hexane--all preheated to 120 F--are fed to the center, top, and bottom of a rotating disc contactor. Rates are controlled by metering pumps. The contactor is 3 feet in diameter by 16 feet high, with 24 contacting stages.

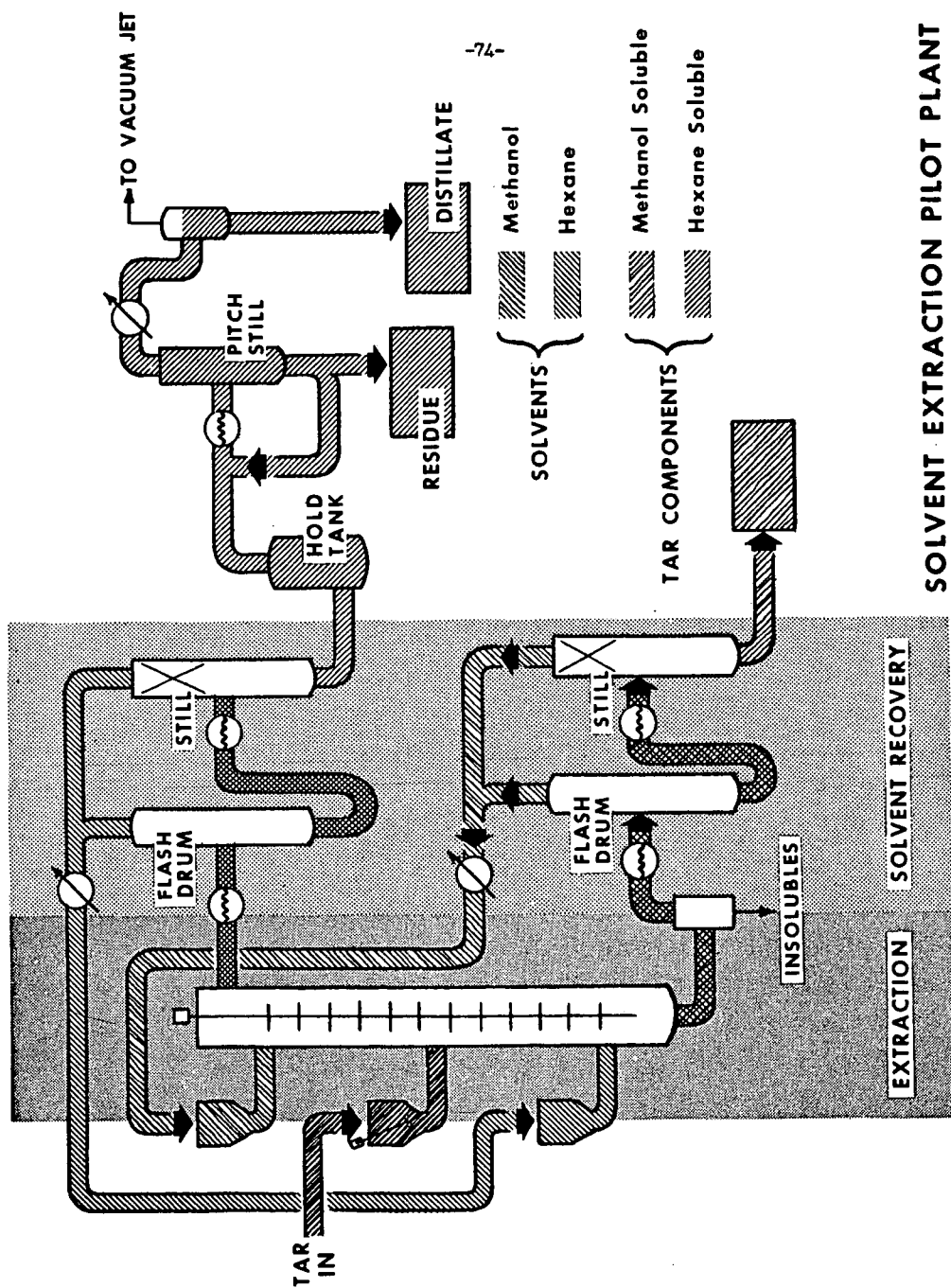
The hexane solution leaves the top of the contactor, passes through a steam heater, then into a flash drum where a substantial portion of the solvent is flashed off. The partially stripped liquid passes through another heater and is fed to a packed tower for the distillation of the remaining solvent. The streams of solvent vapor are combined and passed through a condenser where the water flow is regulated to maintain the proper temperature of the recycled solvent. The solvent-free hexane extract goes to an accumulator tank, then through an electric heater to a vacuum still in which sufficient distillate is taken overhead to yield as bottoms a pitch of the desired softening point. The distillate is topped in another column, not shown on the diagram, to produce a light distillate and a bottoms of the desired flash point and boiling range.

The methanol solution similarly is stripped of solvent in two stages, and the recovered solvent is recycled to the contactor. Adjustment of the water content is necessary because part of that originally present in the solvent feed stream is decanted from the solvent-free material leaving the bottom of the methanol recovery still.

When desired, the methanol-soluble material may be separated into low- and high-boiling fractions in the same column mentioned above for final splitting of the hexane-soluble distillate. Normally, tar acids through the xylenols are taken overhead in this operation. Tables 3 through 7 give typical inspections of the five products resulting from this kind of operation.

#### ACKNOWLEDGMENT

The lignite tar project was set up in a rather unusual manner. The Texas Power & Light Company and the Aluminum Company of America co-operated in the installation and operation of the carbonizer at Rockdale, and jointly sponsored the start of the research project at Battelle. In addition to this, eleven companies participated in the tar research. In return for nominal support of the research costs, they had access to the results of our work, contributed helpful information and suggestions during the course of the research, and were expected to conduct further work in their own laboratories.



## SOLVENT EXTRACTION PILOT PLANT

TABLE 3.

PROPERTIES OF FORERUN, DISTILLING TO 200 C, OF DISTILLATE  
OF HEXANE SOLUBLES OF PRIMARY LIGNITE TAR

Specific Gravity, 25/25 C	0.8503
Refractive Index, $n_D^{25}$	1.4754
Viscosity, kinematic cs, 100 F	1.11
Flash Point, F	90
Fire point, F	165
Copper Strip Corrosion	No discoloration
Pour Point, F	<-70
Tar Acids, volume per cent	1.7
Tar Bases, volume per cent	1.2
Neutral Oil, volume per cent	97.1
Paraffins, volume per cent	14
Olefins, volume per cent	41
Aromatics, volume per cent	45
Elemental Composition, per cent, water-free basis	<div> <div>C</div> <div>H</div> <div>N</div> <div>S</div> <div>O(diff)</div> </div> <div> <div>85.4</div> <div>11.7</div> <div>0.2</div> <div>1.6</div> <div>1.1</div> </div>
Distillation, ASTM D20-52, weight per cent	
To 170 C	26.7
170-235 C	62.1
235-270 C	7.7
270-300 C	2.3
300-355 C	0.8
Residue at 355 C	0.3
Loss	0.1
Residue at 300 C	1.1
Decomposition Temperature, C	>355

TABLE 4.

PROPERTIES OF DISTILLATE, TOPPED TO 200 C, OF HEXANE  
SOLUBLES OF PRIMARY LIGNITE TAR

Specific Gravity, 25/25 C	0.9325										
Refractive Index, $n_D^{25}$	1.5242										
Viscosity, kinematic cs, 100 F	8.13										
Flash Point, F	208										
Fire Point, F	320										
Copper Strip Corrosion	No discoloration										
Pour Point, F	66.5										
Tar Acids, volume per cent	7.7 ± 2										
Tar Bases, volume per cent	1.6										
Neutral Oil, volume per cent	90.7 ± 2										
Paraffins, volume per cent	15										
Olefins, volume per cent	39										
Aromatics, volume per cent	46										
Elemental Composition, per cent, water-free basis	<table><tr><td><u>C</u></td><td><u>H</u></td><td><u>N</u></td><td><u>S</u></td><td><u>O(diff)</u></td></tr><tr><td>85.4</td><td>10.7</td><td>0.4</td><td>1.0</td><td>2.5</td></tr></table>	<u>C</u>	<u>H</u>	<u>N</u>	<u>S</u>	<u>O(diff)</u>	85.4	10.7	0.4	1.0	2.5
<u>C</u>	<u>H</u>	<u>N</u>	<u>S</u>	<u>O(diff)</u>							
85.4	10.7	0.4	1.0	2.5							
Distillation, ASTM D20-52, weight per cent											
To 170 C	0.1										
170-235 C	14.3										
235-270 C	20.1										
270-300 C	18.1										
300-355 C	27.7										
Residue at 355 C	18.6										
Loss	1.1										
Residue at 300 C	46.3										
Decomposition Temperature, C	>355										

TABLE 5.  
PROPERTIES OF RESIDUE OF HEXANE SOLUBLES OF  
PRIMARY LIGNITE TAR

Softening Point, Ring and Ball, C	68
Penetration, 100 g, 5 sec, 77 F	1
Viscosity, SFS, 350 F	39
C-I, per cent	0.36
Nitrobenzene Insoluble, per cent	1.1
Ash, per cent	0.1
Specific Gravity, 25/25 C	1.064
Elemental Composition, per cent, water- and ash-free basis	<div> <div>C</div> <div>H</div> <div>N</div> <div>S</div> <div>O(diff)</div> </div> <div> <div>87.6</div> <div>7.6</div> <div>0.7</div> <div>0.8</div> <div>3.2</div> </div>
Distillation, ASTM D20-52, weight per cent	
To 300 C	4.0
300-Decomposition Temperature	13.4
Residue at Decomposition Temperature	82.6
Loss	--
Residue at 300 C	96.0
Decomposition Temperature, C	355

TABLE 6.

PROPERTIES OF LOW-BOILING METHANOL SOLUBLES, DISTILLING  
UNDER 235 C, OF PRIMARY LIGNITE TAR

Caustic Soluble, per cent	99
Specific Gravity, 25/25 C	0.991
Viscosity, kinematic cs, 100 F	3.17
Sulfur Content, per cent	0.13
Nitrogen Content, per cent	0.67
Distillation, ASTM D20-52, weight per cent	
To 170 C	0.0
170-235 C	81.3
235-270 C	8.8
270-Decomposition Temperature	6.3
Residue at Decomposition Temperature	2.4
Loss	1.2
Residue at 300 C	2.4
Decomposition Temperature, C	280

TABLE 7.

PROPERTIES OF HIGH-BOILING METHANOL SOLUBLES, BOILING  
OVER 235 C, OF PRIMARY LIGNITE TAR

Specific Gravity, 25/25 C	1.163
Viscosity, SFS, 350 F	12
Softening Point, Ring and Ball, C	40-43
Sulfur Content, per cent	0.99
Nitrogen Content, per cent	1.61
Distillation, ASTM D20-52, weight per cent	
To 170 C	0.1
170-235 C	11.3
235-270 C	12.7
270-300 C	24.1
300-Decomposition Temperature	8.5
Residue at Decomposition Temperature	40.9
Loss	2.4
Residue at 300 C	49.4
Decomposition Temperature, C	325

The companies participating were:

Barrett Division  
Celanese Corporation  
Grace Chemical Company  
Koppers Company, Inc.  
The Merichem Company  
Oil and Chemical Products, Inc.

Olin Mathieson Chemical Corporation  
Reilly Tar and Chemical Corporation  
Spencer Chemical Company  
Union Carbide Olefins Company  
Western Tar Products Corporation

We gratefully acknowledge their assistance and their willingness to have this information presented. We also express our appreciation to the sponsoring companies, Texas Power & Light and Alcoa, for permission to present this information, and for the understanding and assistance we have received in the course of more than five years of a fine relationship.

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STUDIES ON LOW-TEMPERATURE LIGNITE TAR  
II. CHARACTERIZATION OF MATERIALS OTHER THAN TAR ACIDS

by

E. Jack Kahler, D. C. Rowlands\*, and W. C. Ellis  
Battelle Memorial Institute  
Columbus, Ohio

As described in the first paper of this series, primary tar from the low-temperature carbonization of lignite can be processed in a number of different ways. The various products obtainable contain a wide assortment of chemicals and classes of chemicals in different combinations. The purpose of this paper is to describe what has been learned about the different classes of chemicals in primary tar. The major effort was directed toward identifying the classes of the chemicals rather than searching out the identities and quantities of individual components. However, some individual compounds were studied in the process.

The most important single characteristic of low-temperature tar is that usually, for each class of compounds found, all the homologues are present. However, no one compound is present in a large amount. In the primary tar, as received, phenol is the most abundant single compound, in about one per cent.

Primary Tar

Primary tar is composed of materials that distill at temperatures from below 100 C to about 350 C, as well as high-molecular-weight, pitch-like materials. All characterization work has been done on distillates. However, it is believed that the residual material probably has the same general proportions of chemical compound classes as do the distillable fractions.

Primary tar is composed of tar acids, tar bases, and neutral oil as determined by their relative solubility or insolubility in caustic or dilute acid. The solvent-extraction process described in Paper I of this series divides the primary tar so that most of the tar acids are soluble in the

\*Present address: Chemical Abstracts, Columbus, Ohio

methanol-water phase, and most of the neutral oil is soluble in the hexane phase; the tar bases are divided quite evenly between the two phases.

Figure 1 shows the boiling point, refractive index, and density curves obtained from a vacuum fractional distillation of a vacuum-flash distillate of a primary tar studied early in the program. The individual fractions were composited to fifteen fractions. All of these, except for the lowest boiling composites, contained about the same proportions of tar acids, tar bases, and neutral oil. The fall in refractive index and corresponding rise in density has not been explained or studied. These effects might have resulted from azeotrope formation because neither tar acids nor neutral oil showed this effect when they were distilled separately. The average composition of distillates of lignite tar is as follows:

Tar acids	25 - 30 per cent
Tar bases	4 - 5 per cent
Neutral oil	65 - 70 per cent

The remainder of this paper and subsequent papers in the series describe what was learned when these three classes of tar constituents were studied individually.

#### Tar Acids

Tar acids, or those materials soluble in caustic, were found to be primarily phenolic compounds with no more than two per cent of aliphatic carboxylic acids. For this work, tar acids were divided into two parts: low-boiling tar acids and high-boiling tar acids. The dividing atmospheric boiling point was 235 C, as this temperature is slightly higher than the 225 C boiling point of the least volatile xyleneol (3,4), and thus insures the inclusion of all the xyleneols in the low-boiling tar acids. The separation was generally made by distilling off the low-boiling tar acids under vacuum in a nitrogen atmosphere. The high-boiling tar acids were sometimes distilled at temperatures up to those equivalent to 300 to 350 C at atmospheric pressure. In such cases, only about 50 to 60 per cent of the high-boiling tar acid fraction distilled.

The composition of the low-boiling tar acids was studied by infrared analysis after the acids had been converted to their methyl ethers. This work is described in detail in Paper III of this series. Phenol was found to be the most abundant single tar acid. All of the cresols, xyleneols, and ethylphenols were also present in low-boiling tar acids.

The high-boiling tar acids distilling up to 335 C were also studied. This work is described in detail in Paper IV of this series. Alkylated phenols, naphthols, indanols, and polyhydroxylic phenols were the predominant classes of compounds found in high-boiling tar acids.

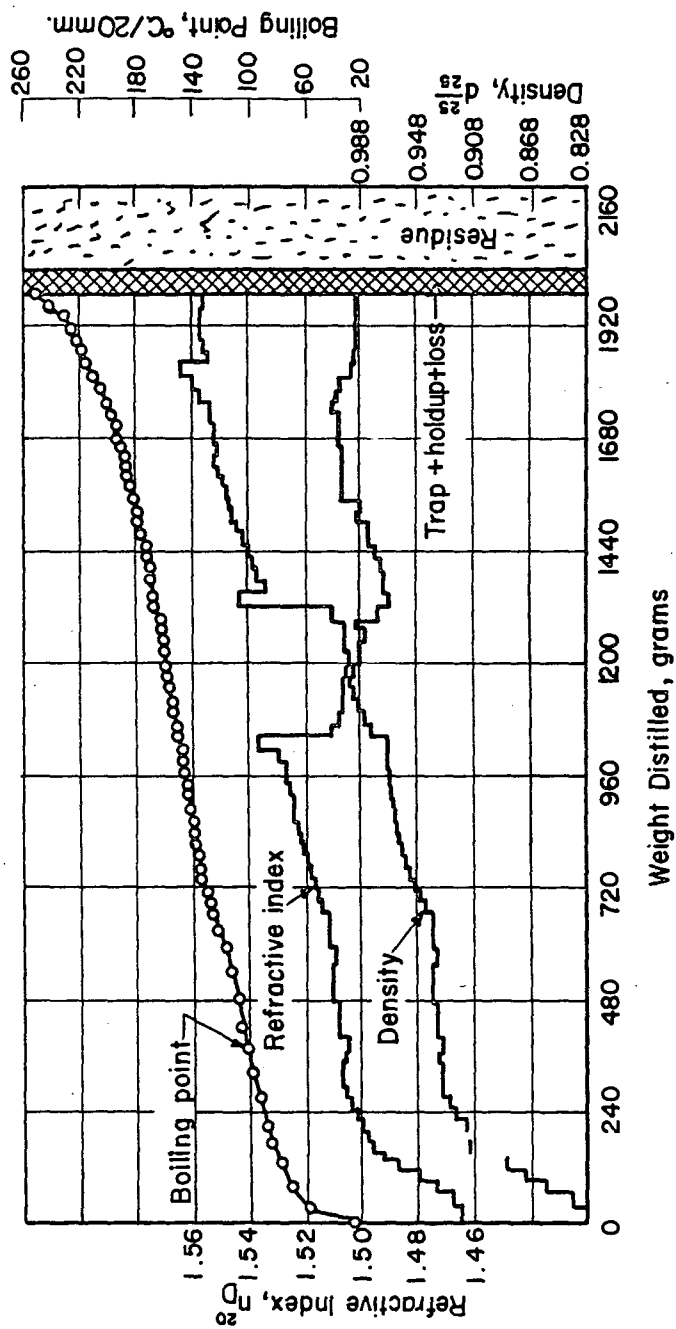


FIGURE 1. FRACTIONATION BY DISTILLATION OF VACUUM-FLASH DISTILLATE

### Tar Bases

Tar bases, or those materials soluble in dilute mineral acid, are present in tar distillates to the extent of only 3.5 to 4.5 per cent. As they represent only a small part of the tar, only limited studies were made of their nature. Actually, all of the tar bases cannot be easily recovered, and yields of less than 1.5 per cent were realized by conventional recovery methods. Distillations, spot tests, and paper chromatography indicated that tar bases are primarily nitrogen heterocyclics of the pyridine and quinoline types. No evidence was obtained of aniline derivatives.

### Neutral Oil

Neutral oil, which represents more than two-thirds of primary tar, is composed primarily of hydrocarbons. These hydrocarbons are paraffins, olefins, and aromatics. Also present are nonacidic "polar compounds" which contain oxygen, sulfur, or nitrogen. Figure 2 shows the results of fractionating neutral oil in a Podbielniak Hypercal distillation unit. Evidence of some degree of separation is shown by the plateauing in the boiling-point curve and the periodic rise and fall of the refractive index curve. Infrared studies of selected fractions showed those corresponding to the maxima of the refractive index curve to be predominantly aromatic, and those corresponding to the minima to be predominantly aliphatic. The periodicity is evidence for the homologous nature of the chemicals in primary tar.

Silica-gel-displacement chromatography was used to assay neutral oil for content of paraffins, olefins, and aromatics. Figure 3 shows a typical curve obtained by the method of Dinneen, et al.<sup>(1,2)\*</sup>. These results are compared in Table 1 with those obtained by a conventional sulfuric acid extraction method as described by Reynolds and Holmes.<sup>(3)</sup> There is no satisfactory explanation for the remarkable differences in the paraffin and aromatic values obtained by the two methods. However, the polar compounds, which are believed to be present in about 20 per cent, could be the source of difference. They are classed as "aromatics" by the silica gel method, and as olefins in the sulfuric acid method.

The various classes of compounds in neutral oil have been separated and studied for the types of structures present. Infrared spectroscopy has been the chief analytical technique used for identification of structural features.

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\*References are located at the end of this report.

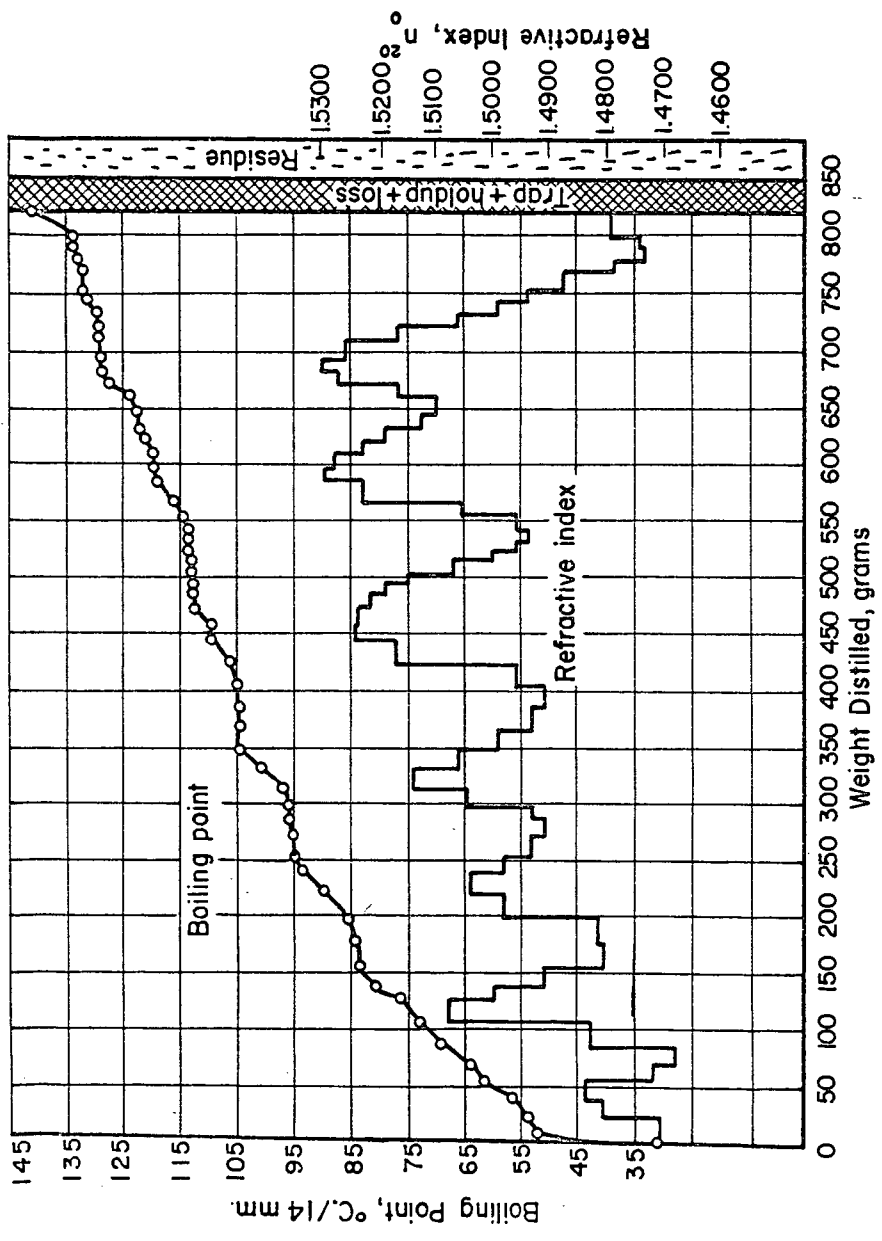


FIGURE 2. PRECISION FRACTIONATION OF NEUTRAL OILS

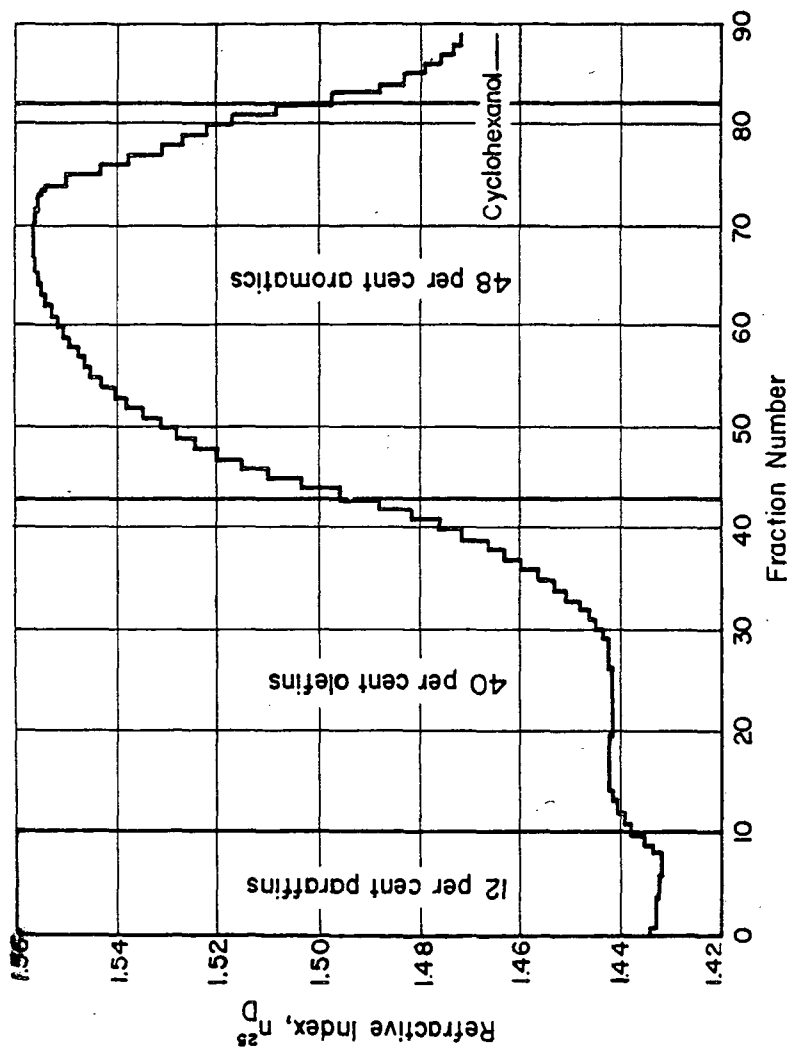


FIGURE 3. SILICA-GEL ADSORPTOGRAM FOR 35 PER CENT NEUTRAL OIL

TABLE 1. COMPOSITION OF NEUTRAL OIL

Component	Method of Analysis	
	H <sub>2</sub> SO <sub>4</sub>	Si Gel
Paraffins	33	11-13
Olefins	43	35-40
Aromatics	24	48-53

### Paraffins

The paraffins in lignite tar are primarily straight-chain hydrocarbons with a small amount of branching. The location of the branching in the paraffins is not known, but it is probably random. About one-third of the paraffins form an adduct with urea. This indicates that the adducted paraffins are either unbranched or that the branching is close to the end of the hydrocarbon chain. Hydrocarbon ring analysis based on physical properties showed that the paraffins and olefins combined contain about 20 per cent ring carbon atoms.

Paraffins were isolated from high-boiling fractions of neutral oil as colorless waxes. Although considerable efforts were made to purify these waxes to yield high-melting solids, the highest melting-point range attained was 40 to 47 C. Infrared and elemental analyses of these waxes showed them to contain only carbon and hydrogen.

### Olefins

Early infrared studies on selected olefin fractions, separated from neutral oil by silica gel, showed the three major kinds of olefins present to be terminal or alpha, trans-internal, and tertiary.

To learn more about the olefins, a study was made of the effect of various strengths of H<sub>2</sub>SO<sub>4</sub> on the removal of olefins. Figure 4 shows how the percentage of neutral oil extracted rises as stronger H<sub>2</sub>SO<sub>4</sub> is used, a sharp rise taking place at 70 per cent acid. At this acid strength, the bromine number begins to drop rapidly. The material extracted by the more dilute acids is believed to be mostly polar compounds (discussed in a later section). Figure 5 shows a silica-gel curve of neutral oil washed with cold 78 per cent H<sub>2</sub>SO<sub>4</sub>. The proportion of olefins remaining was slightly higher than in the original neutral oil. Table 2 shows the calculated amounts and the proportions of the paraffins, olefins, and aromatics that were extracted by the acid.

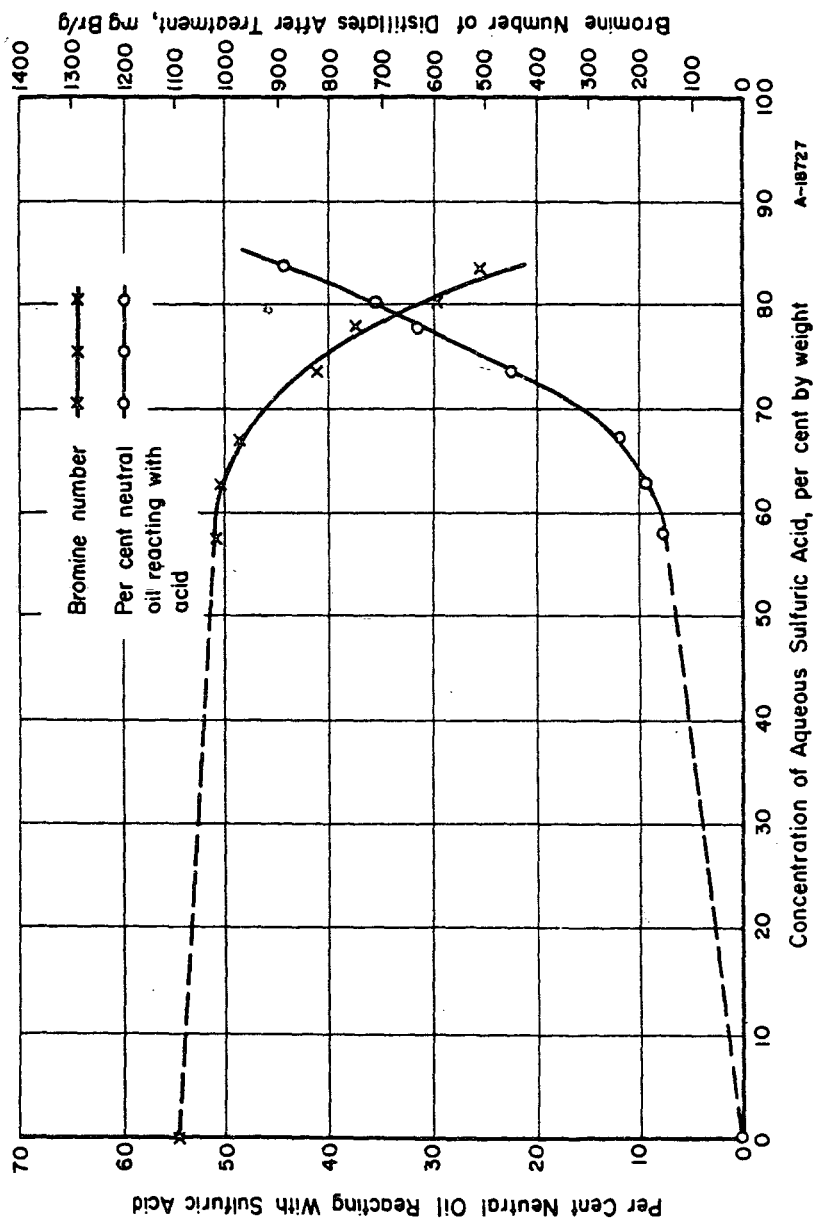


FIGURE 4. EFFECT OF VARIOUS STRENGTHS OF SULFURIC ACID ON NEUTRAL OIL

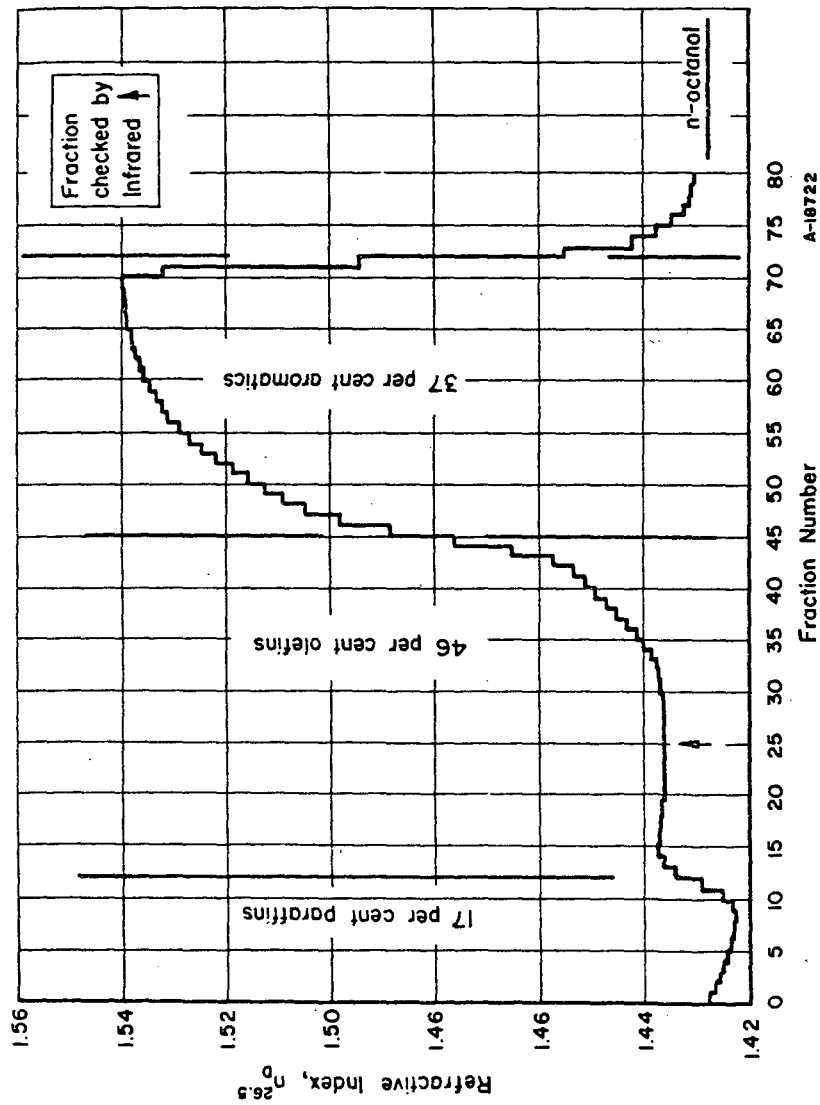


FIGURE 5. SILICA-GEL ADSORPTOGRAM FOR NEUTRAL OIL WASHED WITH COLD 78 PER CENT SULFURIC ACID

TABLE 2. COMPOSITIONS OF NEUTRAL OIL BEFORE AND AFTER  
BEING WASHED WITH COLD 78 PER CENT  $H_2SO_4$

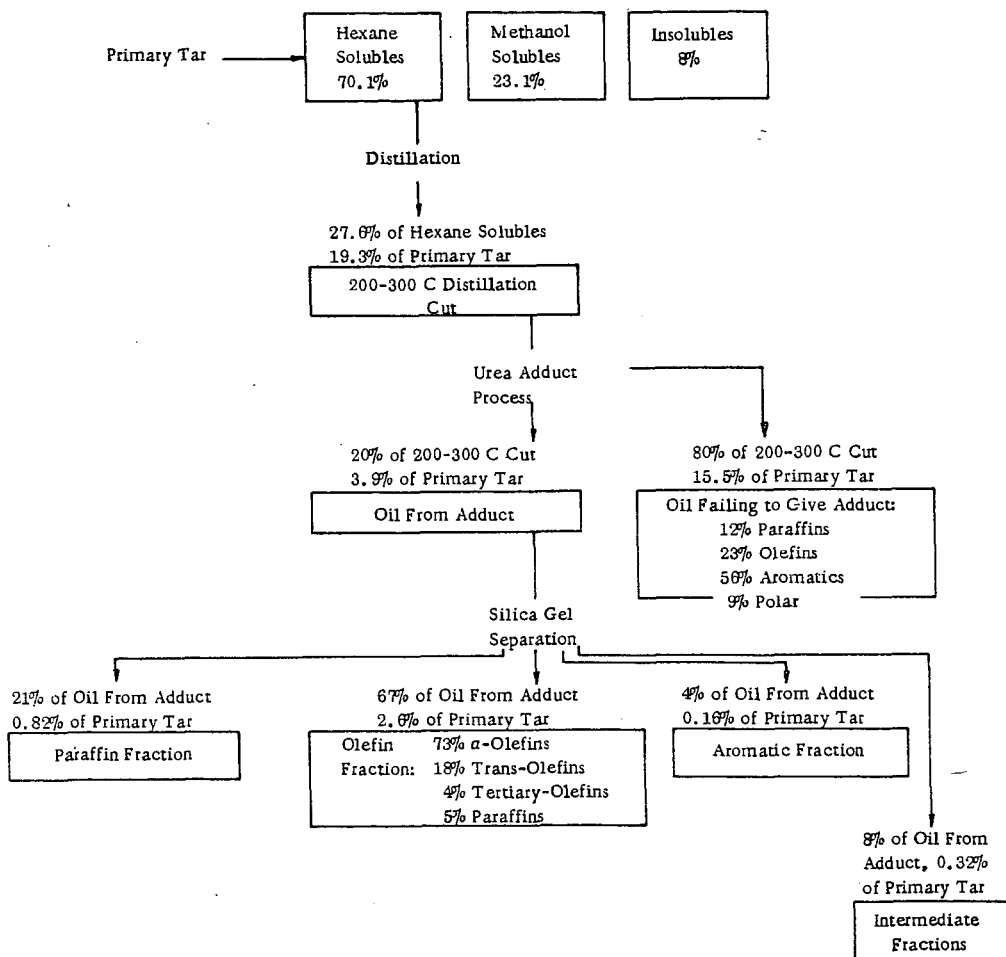
	Neutral Oil Components <sup>(a)</sup> , per cent			Total
	Paraffins	Olefins	Aromatics	
Original neutral oil	12	40	48	100
Washed neutral oil	11.6	31.3	25.2	68.1
Amount removed	0.4	8.7	22.8	31.9
Percentage of composition removed material	1+	27+	71+	--

(a) Determined by displacement silica gel chromatography.

About one-half of the olefins present in lignite tar are  $\alpha$ -olefins. Because the double bond is located at the end of the molecule,  $\alpha$ -olefins can form adducts with urea providing the remainder of the chain is not branched. This urea reaction, together with the selective separation of paraffins and olefins on silica gel, provided a means of obtaining enriched samples of  $\alpha$ -olefins. Figure 6 shows how  $\alpha$ -olefins were separated from a 200 to 300 C cut of hexane solubles obtained from the solvent extraction process. The laboratory separation described yielded a water-white olefin fraction which was about 75 per cent  $\alpha$ -olefin. Some trans- and tertiary-olefins were also present.

The individual small fractions obtained from the silica-gel separation of the olefins from the whole adducted oil were subjected to further study. Table 3 shows the information gained about average molecular weight, ratio of  $\alpha$ -olefins to total olefins, and total double bonds per molecule as determined by infrared and by bromine number. The average length of the olefin chains ranged from 14 to 16 carbon atoms, with most of the fractions containing about one double bond per molecule. Earlier olefin fractions contained somewhat less unsaturation, which was probably evidence of incomplete separation of paraffins from the olefins. Later olefin fractions contained somewhat more unsaturation which could be evidence of multiple unsaturation, although no infrared evidence was found of conjugated unsaturation. As these olefins had adducted with urea, this might be interpreted to suggest the presence of diolefins in which both double bonds are located terminally.

No work was done to prove the presence or absence of cyclic olefins in neutral oil, although such compounds are expected to be present. A ring analysis was made of the combined paraffin-olefin fraction, as separated by silica gel, of a 200 to 300 C cut. Various physical measurements were used as recommended by Deanesley and Carleton<sup>(4)</sup> to calculate the results, which



N-56563

FIGURE 6. SEPARATION OF A 200-300 C BOILING CONCENTRATE OF  $\alpha$ -OLEFINS FROM PRIMARY TAR

indicated about one-fourth of the carbon atoms were naphthenic. This same fraction was found by infrared to contain 61 per cent olefins.

TABLE 3. CHARACTERIZATION OF SILICA-GEL CHROMATOGRAPHY CUTS OF OIL FROM UREA ADDUCT OF DISTILLATE OF HEXANE SOLUBLES

Fraction	Refractive Index, $n_D^{20}$	Comments(a)	Molecular Weight(b)	Ratio of $RCH=CH_2$ (Alpha) Olefins to Total Olefins(c)	Total Double Bonds/Mol by infrared	Total Double Bonds/Mol by Bromination(d)
1	1.4344	↑ Paraffins				0.0
2	1.4336					
3	1.4328					
4	1.4322	↓ Intermediate				
5	1.4317					
6	1.4337					
7	1.4385	↑	233	0.74	0.6	0.7
8	1.4389					
9	1.4387					
10	1.4386	↑	225	0.78	0.8	0.8
11	1.4386					
12	1.4388					
13	1.4387	↑	215	0.77	0.9	0.9
14	1.4390					
15	1.4392					
16	1.4393	↓ Olefins 67 Per Cent	209	0.77	1.0	1.0
17	1.4396					
18	1.4397					
19	1.4399	↓	206	0.77	1.0	1.1
20	1.4401					
21	1.4412			0.75	1.1	
22	1.4458	↓ Intermediate	198	0.75	1.3	1.2
23	1.4604					
24	1.4855					
25	1.4382	↑ Aromatics				
26	1.4330					

(a) Based on  $n_D^{20}$  and infrared spectroscopy.

(b) Determined cryoscopically in benzene.

(c) Determined by infrared spectroscopy. The olefins other than  $\alpha$ -olefins remained about 75 per cent trans ( $HC=CH$ ) and 25 per cent tertiary ( $R_1R_2C=CH_2$ ) from fraction to fraction.

(d) Br-BrO<sub>3</sub> method, ASTM D1158-55T (1955). Values under 1 probably indicate paraffin contamination whereas values over 1 may indicate a small amount of multiple unsaturation.

### Aromatics

A concentrate of aromatics was obtained from neutral oil by the use of butyrolactone as selective solvent. The aromatic fraction was further purified by the use of silica gel and sodium amide in attempts to remove nonaromatics and particularly the polar compounds. The material was

carefully rectified at reduced pressures into 45 fractions over a calculated atmospheric boiling point range of 140 to 290 C. Table 4 summarizes the types of hydrocarbons definitely identified by infrared analysis of the individual fractions. Polar compounds were evident in the higher boiling fractions. Benzofuran and 2-methylbenzofuran were tentatively identified as major nonhydrocarbon contaminants.

TABLE 4. SUMMARY OF HYDROCARBON TYPES FOUND BY INFRARED SPECTROSCOPY IN FRACTIONS OF REFINED AROMATIC CONCENTRATE

Boiling Range, C/1 atmos.	Characterization
140-163.0	Principally xylenes
157.1-181.5	C <sub>9</sub> aromatics, principally trimethyl benzenes
175.5-205.0	C <sub>9</sub> and higher aromatics including indene and hydrindene
202.0-230.5	Naphthalene plus other aromatics
222.5-251.5	Methyl naphthalenes
247.5-290.5	Possibly dimethyl naphthalenes plus other aromatics

Ring analysis of the aromatic concentrate based on physical properties showed the average structure to correspond to methyl- or ethyltetralin. However, this figure may be in error because of polar contaminants. There was little evidence of any significant amount of polynuclear aromatics or long-chain alkylaromatics. Even though special efforts had been made to remove nonhydrocarbon contaminants, elemental analysis showed the concentrate to contain sulfur, nitrogen, and oxygen (by difference). If the nonhydrocarbon material had the same average molecular weight as the aromatics with one hetero atom per molecule, the various contaminants would be present as follow:

Hetero Atom	Elemental Percentage in Concentrate	Calculated Contaminant Percentage
S	2.4	12.1
N	0.2	2.5
O	1.6	16.1

These figures total 30 per cent and may be high, as oxygen was figured by difference.

### Polar Compounds

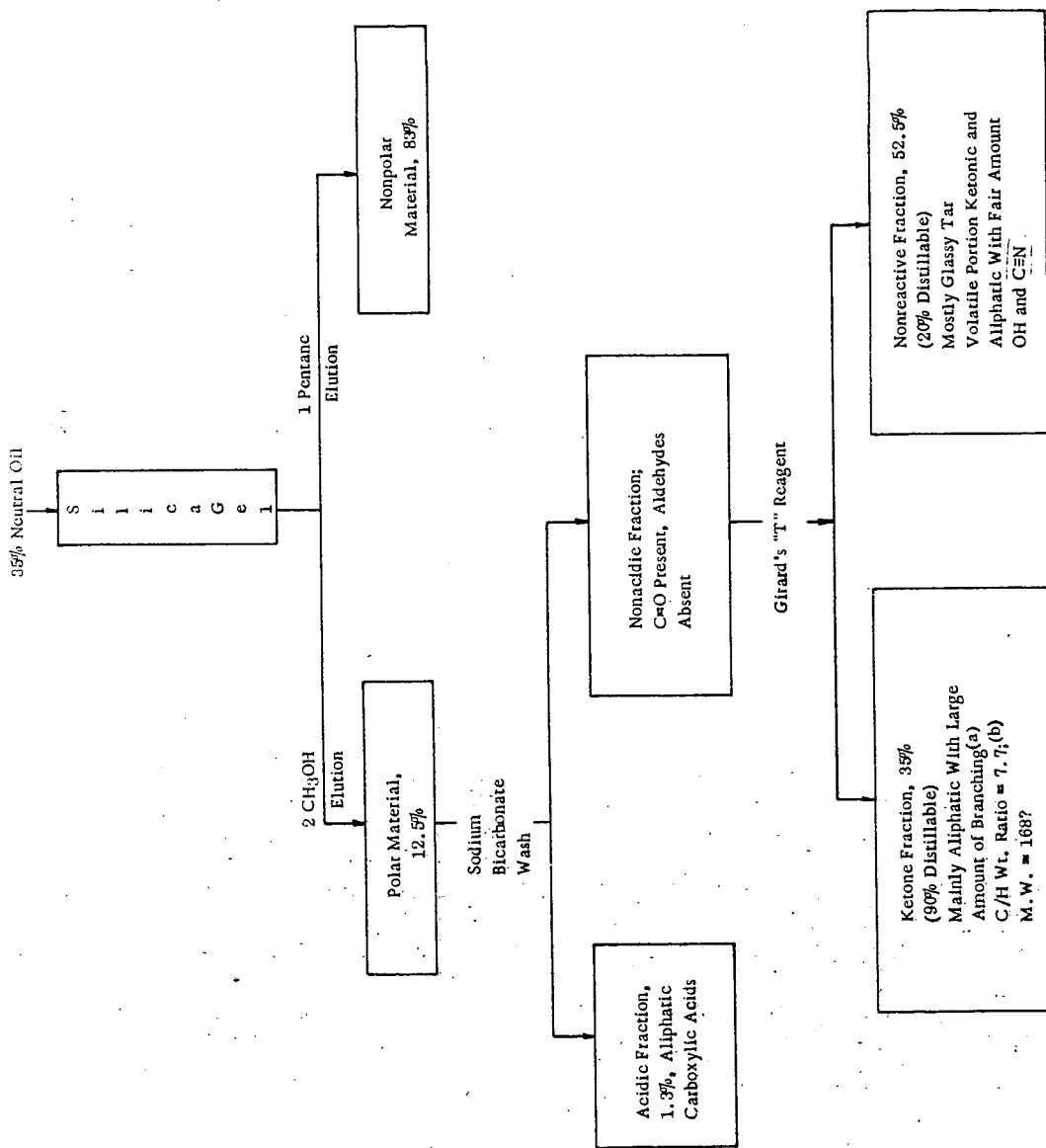
A number of separation methods were applied to neutral oil in attempts to obtain polar compounds free of hydrocarbons. The only method that was reasonably successful involved use of silica gel and elution chromatography as shown in Figure 7. Although other information suggests that neutral oil contains about 20 per cent of polar compounds, only 12.5 per cent was isolated by this particular method.

Infrared indicated that imino, hydroxyl, and cyano groups were present in these polar compounds. However, the major chemical class was ketones. Further concentration and study of the ketones showed the distillable ketones to be primarily aliphatic with a large amount of branching. It will be shown in Paper IV that ketones are the principal contaminant in tar acids.

Sulfur-containing compounds are also present in polar compounds, but spectral evidence is not satisfactory for identification of most classes of sulfur compounds. Furthermore, although chromatography is often effective for the separation of sulfur compounds from hydrocarbons, the sulfur compounds in lignite tar could not be cleanly separated by this technique. It has been found that the sulfur compounds in lignite tar are chemically quite unreactive. Reactive compounds such as thiols and disulfides appear to be present, but in relatively low concentration as compared with aliphatic and cyclic sulfides. Thiophenes were not present; since they are relatively strong infrared absorbers, any significant amounts would have been detected.

### Summary

Chemically, primary tar is composed of about 26 per cent tar acids, 4 per cent tar bases, and 70 per cent neutral oil. The make-up of Texas lignite tar by classes of chemicals is summarized in Table 5. Considerably more effort will be needed to obtain more detailed data. This is particularly true for the constituents in the high-boiling fractions of the tar. In any one of the classes of chemicals, a large number of individual chemical compounds are present.



(a) Iodoform test negative.

(b) The C/H ratio of an aliphatic ketone in this range is about 6.0 whereas benzophenone has a C/H ratio of 15.6

FIGURE 7. STUDY OF POLAR MATERIAL IN 35 PER CENT NEUTRAL OIL

TABLE 5. SUMMARY OF CHEMICAL CLASSES IN TEXAS LIGNITE TAR

Tar acids 26%	Low-boiling - 5% - phenols, cresols, xylenols, ethylphenols High-boiling - 21% - phenols, naphthols, indanols, polyhydroxylic phenols
Neutral oil 70%	Paraffins - 10% - straight chain, lightly branched Olefins - 25% - alpha, trans-internal, tertiary Aromatics - 21% - benzenes, naphthalenes, hydrindenes, indenenes Polar compounds - 14% - ketones, sulfides, nitriles
Tar bases 4%	Heterocyclics - 4% - pyridines, quinolines

#### ACKNOWLEDGMENT

In addition to the acknowledgments given in the first paper of this series, appreciation goes to M. M. Baldwin and H. R. Batchelder for their assistance in the guidance of the work. The considerable help from the infrared work of Josephine Brewer and Clara D. Smith is also recognized.

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STUDIES ON LOW-TEMPERATURE LIGNITE TAR  
III. STUDY OF LOW-BOILING TAR ACIDS

by

J. Brewer and Clara D. Smith\*  
Battelle Memorial Institute  
Columbus, Ohio

This paper will describe the analysis of the lignite tar-acid fraction boiling below 235 C to determine the relative amounts of phenol, cresols, xylenols, and ethyl phenols in low-boiling tar acids. Some work has been previously described in the literature with respect to the analysis of alkyl phenols in the range of the low-boiling tar acids. Recently the emphasis has been on gas-phase chromatography or a combination of gas-phase chromatography and infrared.<sup>(1, 2, 3, 4)\*\*</sup> However, this technique was not available at the time the analysis was needed. Shortly after this work had been completed, a paper by Fair and Friedrich<sup>(5)</sup> was published concerning the analysis of alkyl phenol mixtures by infrared. The present work differs from that of Fair and Friedrich and other previous work on tar acids<sup>(6, 7, 8)</sup> in that, by this method, the tar acids are converted into methyl ethers and the analysis carried out on the ethers.

The conversion to methyl ethers minimizes the possibility of ambiguities due to thermal and oxidative effects and has several advantages from an infrared point of view. It eliminates a band-overlap problem encountered with the free acids and gives materials that are liquid at room temperature, eliminating the need for solvents.

Experimental Procedure

A crude distillate was caustic washed, the separated sodium derivatives benzene extracted, and the tar acids then sprung with acid. The reconstituted tar acids were methoxylated according to the method of Rowe and Bannister, et al.<sup>(9)</sup>, and the unconverted portion subjected to a second treatment. The combined yield was 95 per cent. Infrared showed little difference in the two sets of ethers, which indicated that methylation had not concentrated any particular tar-acid ether. The methyl ethers were

\*Present Address: Infrared Spectroscopist at Evansville, Indiana.

\*\*The superscript numbers refer to literature references listed at end of paper.

combined and fractionally distilled through a Podbielniak Hypercal column at reflux ratios of 20/1 to 40/1 at one atmosphere under nitrogen. Seventy-seven cuts were taken up to the boiling point of 3,4-xylenol methyl ether, the highest boiling isomer. The boiling points of the cuts were plotted against weight per cent of the charge distilled as shown in Figure 1. Even when the distillation was taken to a point corresponding to ten additional cuts, the residue was still fluid, indicating little polymerization or decomposition. However, the material boiling above Fraction 78 consisted of methyl ethers of tar acids with boiling points above the xylenols.

From the boiling-point curve, cuts were chosen for spot checking by infrared.\* At the points on the curve where the boiling point rose sharply, the rise was bracketed by choosing cuts on either side. From the spectra of these cuts, it was determined that cuts in some boiling-point ranges could be recombined for analysis. The first seventeen cuts were anisole (methyl ether of phenol). From the total weight of these cuts, plus a percentage of several following cuts, the per cent of phenol could be easily calculated. Cuts 23 through 53 were combined and analyzed for the three methyl anisole isomers. Cuts 54 through 77, however, necessitated a cut-by-cut analysis for five to six components per cut.

Pure methyl ethers of phenol and the cresols for use as standards were available by direct purchase. Methyl ethers of the xylenols were prepared at Battelle from purchased xylenols. The ethyl phenols had to be both synthesized and methylated at Battelle. For boiling points of the standards, see Table 1.

TABLE 1. ANALYTICAL WAVELENGTHS OF METHYL ETHERS OF LOW-BOILING TAR ACIDS

Methyl Ether	Boiling Range of Known Ethers, C	Analytical Absorption Band, $\mu$	Baseline Used, $\mu$
		$\mu$	$\mu$
Methoxybenzene	152-154	14.47	12.52-14.90
2-Methylmethoxybenzene	170-172	14.01	12.52-14.90
4-Methylmethoxybenzene	173-174	12.23	10.70-13.65
3-Methylmethoxybenzene	175-176	14.49	14.20-14.90
2,6-Dimethylmethoxybenzene	181.5-182.5	9.15	7.50-9.25
2-Ethylmethoxybenzene	184.5-185.5	13.30	12.90-13.90
2,5-Dimethylmethoxybenzene	189.5-190.5	8.68	7.50-9.25
		11.85	11.15-13.45
2,4-Dimethylmethoxybenzene	190.5-191.0	8.14	7.50-9.25
		13.29	13.10-13.70
3-Ethylmethoxybenzene	192.0-193.0	14.41	13.75-14.90
3,5-Dimethylmethoxybenzene	194.5-195.5	9.33	9.20-9.90
4-Ethylmethoxybenzene	195.5-196.0	12.07	11.15-13.45
		8.52	7.40-9.20
2,3-Dimethylmethoxybenzene	195.5-196.0	9.02	7.40-10.40
3,4-Dimethylmethoxybenzene	200.5-201.5	8.30	7.40-10.40

\* The infrared instrument used for this work was a Perkin-Elmer Model 21 Spectrophotometer with sodium chloride optics.

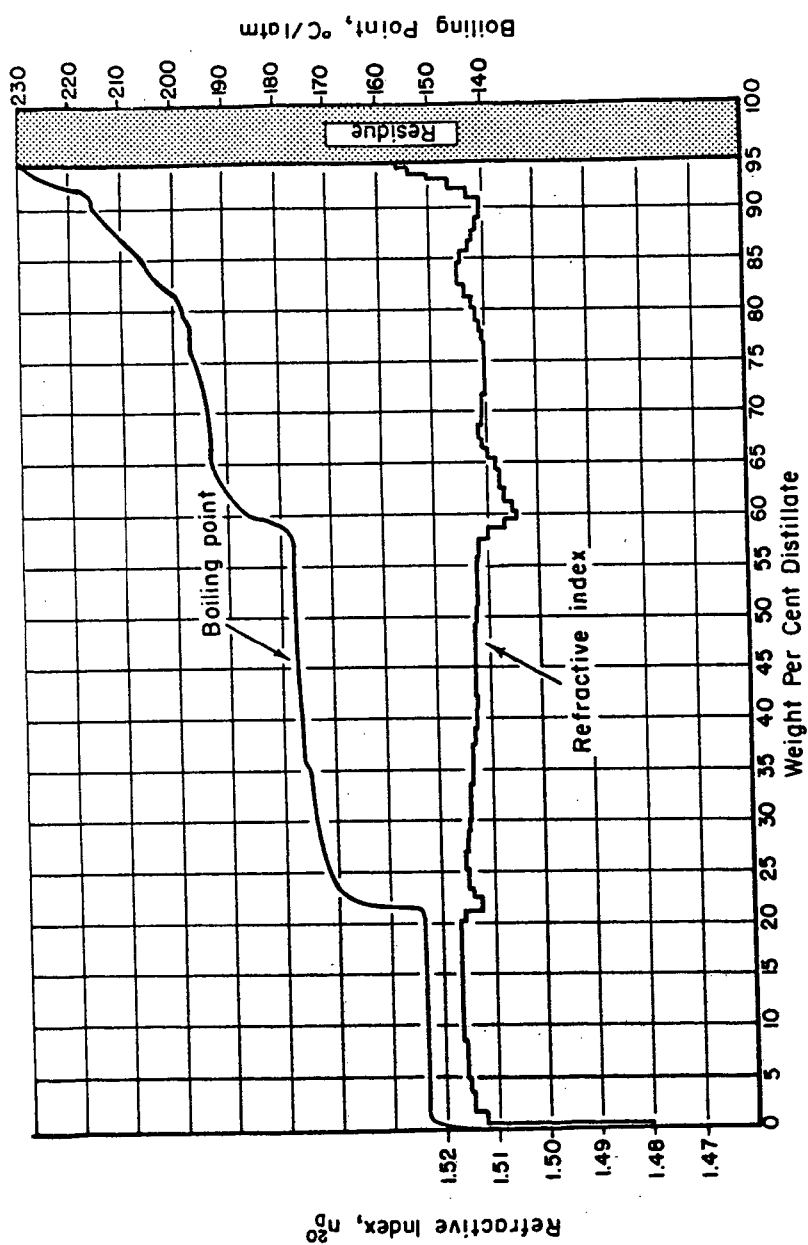


FIGURE 1. FRACTIONATION BY DISTILLATION OF METHYL ETHERS OF LOW-BOILING TAR ACIDS  
A-17579

Spectra were obtained on the standard methyl ethers in the same cell to be used eventually for the samples. A continuous check was maintained on the cell to make certain no change in cell thickness (0.0053 mm) occurred. From the spectrum of each standard methyl ether, a band (or bands) was selected for measurement of the ether in a mixture. The particular wavelength chosen for measurement was selected on the basis of: (1) minimum interference at that wavelength from absorption due to other ethers which, from boiling points, might reasonably be expected to occur in the same cut; (2) a relatively strong band compared with the rest of the spectrum; and (3) conformance with Beer's law as checked by analysis of synthetic blends. The selected wavelengths for each compound are noted in Table 1.

Band intensities at each selected wavelength in standards and samples were measured by the baseline method. Table 2 gives optical densities of the standards at each selected wavelength. Horizontally, across the table the underlined figure is the optical density in the 0.0053-mm cell of the band chosen for analysis. The other figures indicate the relative amount of interference from the other methyl ethers at the selected wavelength. Percentages of individual components were calculated by solution of simultaneous equations. The method of successive approximation was used.

TABLE 2. ABSORPTION COEFFICIENTS AS MEASURED FROM METHYL-ETHER STANDARDS OF XYLENOLS AND ETHYLPHENOLS

Substituted Methoxybenzene	2,6- Dimethyl	2- Ethyl	2,5- Dimethyl	2,4- Dimethyl	3- Ethyl	3,5- Dimethyl	4- Ethyl	2,3- Dimethyl	3,4- Dimethyl
2,6-Dimethyl	<u>.290</u>	-.002	.003	.000					
2-Ethyl	-.108	<u>.602</u>	-.003	.157	-.115				
2,5-Dimethyl (1)	.011	.020	<u>.470</u>	.100	.420	.124	.006		
(2)		-.068	<u>.103</u>	-.007	.006		.048	-.004	
2,4-Dimethyl (1)	.088	.156	.030	<u>.709</u>	.044	-.002	.220		
(2)			.011	<u>.160</u>	-.022	.004	-.005	-.120	
3-Ethyl		.026	-.002	.000	<u>.310</u>	.044	.035	.000	
3,5-Dimethyl			.005	-.004	.048	<u>.437</u>	.007	-.069	.005
4-Ethyl (1)			.012	.000	-.023	<u>.439</u>	<u>.523</u>		
(2)			.026	.041	.020	.060	<u>.330</u>	-.051	.010
2,3-Dimethyl			.014	.017	.000	-.004	.052	<u>.871</u>	.129
3,4-Dimethyl						-.009	.017	.000	<u>.311</u>

The accuracy for this work is probably about  $\pm 10$  relative per cent. The accuracy of the analysis could be considerably improved by use of average optical densities obtained from duplicate or triplicate spectra of samples and standards instead of the single determinations used in this case.

### Results

Table 3 shows the tar-acid composition based on the analysis as performed on the ethers prepared from lignite tar. By calculation, the primary tar used for this work contained about 0.8 per cent of phenol.

TABLE 3. COMPOSITION OF C<sub>6</sub> THROUGH C<sub>8</sub> TAR ACIDS AS CALCULATED FROM INFRARED ANALYSIS OF THEIR METHYL ETHERS

Compound	Relative Amounts of Isomers of Each Type of Tar Acid, weight per cent		Concentration Per Cent of Each Tar-Acid Isomer in Respect to Total Amount of Tar Acids Identified	
Phenol	100	Phenol	27	
2-Methylphenol	29	Cresols	13	44
3-Methylphenol	39		17	
4-Methylphenol	32		14	
2,3-Dimethylphenol	12	Xylenols	3	18
2,4-Dimethylphenol	32		6	
2,5-Dimethylphenol	19		3	
2,6-Dimethylphenol	5		1	
3,4-Dimethylphenol	14		2	
3,5-Dimethylphenol	18		3	
2-Ethylphenol	17	Ethylphenols	2	11
3-Ethylphenol	32		3	
4-Ethylphenol	51		5	

### ACKNOWLEDGMENT

In addition to the acknowledgments given in the first paper of this series, the work of D. C. Rowlands is appreciated for the preparation of the methyl ethers used as standards.

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STUDIES ON LOW-TEMPERATURE LIGNITE TAR  
IV. STUDY OF HIGH-BOILING TAR ACIDS

by

D. C. Rowlands\*, W. H. Powell\*\*, and E. Jack Kahler  
Battelle Memorial Institute  
Columbus, Ohio

Introduction

The purpose of the present work was to obtain enough insight about the constitution of the high-boiling tar acids that the merits of various possible industrial outlets might be properly considered. It was desired to demonstrate the presence of various molecular types in specific vacuum-distillation fractions, and where possible, to make a logical estimate of the proportion in which these types were present.

Summary

Adsorption chromatography paper and gas partition chromatography, nonaqueous titrations to determine average equivalent weights, infrared spectroscopy, mass spectroscopy, and certain specific color reactions to identify classes of tar acids were all used in this study. The types of compounds identified by these techniques are shown in Table 1. No one class of tar acids was predominant, but the presence of the various classes of compounds varied with the boiling range being studied. In general it may be said that the alkyl side chains appeared to consist primarily of methyl and ethyl groups.

\*Present address: Chemical Abstracts, Columbus, Ohio.

\*\*Present address: The Ohio State University, Columbus, Ohio.

TABLE 1. CLASSES OF COMPOUNDS IDENTIFIED IN HIGH-BOILING TAR ACIDS

- 
- |  |
|--|
| (1) Alkylphenols with the total number of alkyl carbon atoms being from 3 to 6                                     |
| (2) Catechol, resorcinol, and hydroquinone and their alkylated derivatives   |
| (3) Trihydric phenols (probably a small quantity)  |
| (4) Indanols and alkylated indanols  |
| (5) Naphthols and alkylated naphthols  |
| (6) Higher molecular weight polynuclear phenols  |
| (7) Ketones (appeared in all 18 distillation fractions of high-boiling tar acids)                                  |
| (8) Indenols and acenaphthols were tentatively identified by mass spectrography in addition to classes noted above |
- 

### Experimental and Discussion

#### Preparation and Preliminary Examination of Tar-Acid-Fractions

A broad cut of crude tar acids was obtained from vacuum-flash distillate of primary tar by caustic extraction. The crude tar acids were distilled under vacuum, and a rough cut (bp 200-335 C/1 atm) was collected for subsequent study. This cut was fractionated at reduced pressure through a 65 x 2.5-cm OD column packed with 1/8-inch glass helices. Atmospheric boiling points at vigorous reflux and refractive indices of the collected fractions are shown in the left-hand portion of Figure 1. The right-hand portion of Figure 1 indicates the results of titrations for carbonylic content by the use of hydroxylamine hydrochloride.<sup>(1)\*</sup> This was attempted after qualitative infrared scanning indicated the presence of carbonylic components. The figures for weight per cent of carbonylic compound were calculated with the aid of molecular-weight approximations based on nitrogen analyses of 2,4-dinitrophenylhydrazones. The presence of compounds which are probably not phenols and possess the carbonyl function was unexpected since the precaution was taken of cross extracting the caustic solution of tar acids during their isolation.

Equivalent weights of the various fractions as shown in the right-hand portion of Figure 1 were determined by nonaqueous titration with sodium methoxide in pyridine<sup>(2)</sup> and have been corrected for content of carbonylic compounds.

\*References are located at the end of this paper.

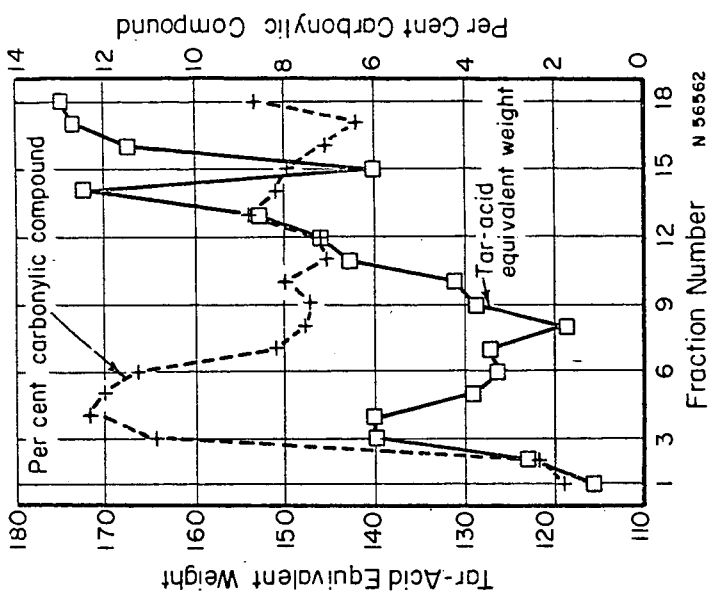
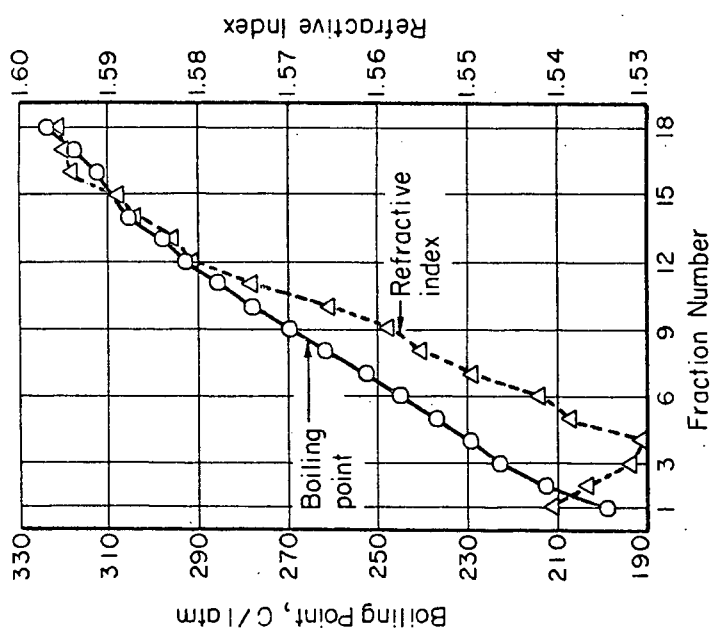


FIGURE I. PROPERTIES OF DISTILLATION FRACTIONS OF HIGH BOILING TAR ACIDS

The tar acid equivalent weights, shown in Figure 1, indicate that the content of dihydric phenols varied with the boiling range, but probably their proportion never exceeded one-fifth of the tar acids in any given boiling range.

It may be noted that tar-acid equivalent weights were reflected to some degree in changes in the refractive indices as presumably were also changes in content of alkyl side chains and concentration of polynuclear phenols.

Tests were made with 2,4,7-trinitrofluorenone reagent<sup>(3,4)</sup> to determine whether appreciable quantities of polynuclear phenols were present in specific distillation fractions. Only a slight positive test was obtained for Fractions 7 through 9; however, Fractions 10 through 18 gave a strongly positive test for polynuclear phenols.

In order to determine the presence of hydro-polynuclear phenols, dehydrogenation experiments combined with ultraviolet characterization of the products were attempted. The method worked well with known compounds, but no dehydrogenation was obtained with Fraction 12, either because the palladium catalyst had been poisoned by sulfur compounds or because no significant amount of hydro-polynuclear phenols was present.

#### Chromatography of Tar-Acid Fractions

Column and partition chromatography were also used in this investigation. Both of these techniques have been used previously to separate mixtures of tar acids.<sup>(5,6,7)</sup> Fraction 3 was selected to determine a procedure, since many of the tar acids boiling in this range had already been identified as described in the previous paper of this series. Infrared examination of each cut obtained from the chromatography of rather large samples (1-10g) on a large column\* showed that, qualitatively, appreciable separation was being achieved. Moreover, the same relative degree of separation was obtained whether the tar-acid methyl ethers\*\* were chromatographed on activated alumina, or the free tar acids on a silicic acid-celite mixture. In fact, a few specific compounds could be identified by characteristic infrared bands. This procedure was sufficient for this relatively low-boiling fraction, but for the higher-boiling fractions, which were more complex, it was necessary to supplement the infrared study of each cut with paper or gas partition chromatography.

First, a study was made of the column and paper chromatography of selected known phenols, both separately and in known mixtures. A one-milligram sample was developed on a 13 x 200-mm column of silicic acid

\*Sizes ranged from 1 x 35-in. to 2 x 67-in. columns.

\*\*Prepared by the method of Woolfolk, Columbia, et al., Bulletin 487, U. S. Bureau of Mines (1950), p. 34.

with 15 per cent ether-petroleum ether. The column was then extruded and streaked with alkaline permanganate solution. All classes of phenols reduce the permanganate to brown  $MnO_2$ . The column was also streaked with a 2 per cent solution of phosphomolybdic acid and exposed to ammonia vapors. It is known that catechol and hydroquinone develop a blue color before exposure to ammonia vapors, whereas all other phenols develop a blue color after exposure to ammonia vapors.<sup>(8)</sup> The band positions in millimeters from the top of the adsorbent are shown in Table 2. It can be seen that a reasonable separation was achieved. Various classes of phenols could be identified from synthetic mixtures.

Known phenols were developed by the ascending method with a benzene-acetic acid-water mixture on a strip of Whatman No. 1 filter paper. This developer is known to separate dihydric phenols easily from alkyl phenols.<sup>(7)</sup> An excellent separation could be achieved, and here identification of individual phenols could be made from synthetic mixtures as shown for three phenols in Table 3. Further, the relative concentration and the amount of substitution of each phenol could be estimated. After these preliminaries, a detailed study of Fractions 6 and 12 was undertaken. Where applicable the same techniques were used for other fractions.

#### Study of Fraction 6 Tar Acids

Fraction 6 of the tar acids was chromatographed on a large silicic acid-celite column and developed gradiently with ether-petroleum ether mixtures. Each of the 300, 10-ml cuts was tested with the phosphomolybdic reagent and ammonia. Dihydric phenols were found in Cuts 176-300. For further study, these cuts were combined systematically into four composites. Table 4 shows the results of the study of each of the composites.

It is known that ortho and para dihydric phenols reduce ammoniacal silver nitrate solution, whereas meta dihydric phenols do not.<sup>(8)</sup> When each composite was tested with this reagent, Composite 3 gave a very faint test and Composite 4 a strongly positive test.

Infrared examination showed that, although each composite was complex, some information relative to compound types could be obtained. For example, it could be shown that the first two composites were structurally similar. They were predominantly alkyl phenols with 4 to 6 side-chain carbon atoms consisting mainly of methyl and ethyl groups. Composite 2 showed less aliphatic CH absorption and had three absorption bands corresponding to 5-indanol. The first three composites all showed a carbonyl contaminant, estimated at about 10 per cent. Composite 4 showed very little aliphatic CH absorption, probably less than an average of two carbon atoms per ring. The aromatic position bands showed 3 or 4 adjacent ring hydrogen atoms, indicating catechol derivatives.

TABLE 2. CHROMATOGRAPHY OF KNOWN PHENOLS ON SILICIC ACID

Phenol	Band Position, mm
Hydroquinone	0-10
Hexylresorcinol	2-8
Catechol	8-20
$\beta$ -Naphthol	30-55
p-Phenylphenol	45-65
5-Indanol	60-90
p-t-Butylphenol	70-100
Octylphenol	95-120

TABLE 3.  $R_f$  VALUES FROM PAPER CHROMATOGRAPHY OF KNOWN PHENOLS WITH BENZENE-ACETIC ACID-WATER (3:3:1)

Phenol	$R_f$ Values	
	Literature <sup>(7)</sup>	Found
Hydroquinone	0.12	0.12
Resorcinol	0.13	--
Catechol	0.36	0.33
4-Methylcatechol	0.46	--
4,5-Dimethylcatechol	0.52	--
3-Methylcatechol	0.60	--
3,4-Dimethylcatechol	0.71	--
3,5-Dimethylcatechol	0.71	--
3-Ethylcatechol	0.80	--
5-Indanol	0.99	0.94
Alkylmonohydric phenols	About 0.99	--

TABLE 4. CHARACTER OF COMPOSITES OF CUTS OBTAINED FROM CHROMATOGRAPHY OF FRACTION 6 ON SILICIC ACID - CELITE

Composite	Cuts	Wt. % Recovered <sup>(a)</sup>	Refractive Index	Ammoniacal AgNO <sub>3</sub> Test	Phosphomolybdic Acid Test		Conclusions
					Before NH <sub>3</sub>	After NH <sub>3</sub>	
1	51-86 <sup>(b)</sup>	48	1.5351	--	--	+	Alkylphenols, indanols, <u>no</u> dihydric phenols
2	87-98	10	1.5472	--	--	+	Same as above, more indanols
3	97-175	21	--	Faintly +	--	+	Alkylphenols and indanols, some dihydric phenols
4	176-319	22	--	+	+	+	Highly substituted mostly dihydric phenols

(a) Over-all recovery. 75 per cent.

(b) The first 50 cuts were only solvent.

TABLE 5. PAPER CHROMATOGRAPHY OF COMPOSITE CUTS OF CHROMATOGRAPHED FRACTION 6 TAR ACIDS

Composite	R <sub>f</sub> Value	Intensity Size Factor	Remarks
1	All on solvent front	--	Alkyl phenols and indanols; no dihydric phenols
2	All on solvent front	--	Same as above
3	0.53	1	Predominantly alkyl phenols and indanols, possibly some substituted catechols
	0.73	1	
	0.81	3	
	0.97	9	
4	0.12	<1	Predominantly catechol and substituted catechols. Small amount of alkyl phenols and/or indanols.
	0.33	4	
	0.45	3	
	0.58	6	
	0.83	2	
	0.97	1	

Table 5 shows the results of paper chromatography of each composite. The intensity-size factor of each spot was a visual estimation and was an indication of concentration. The results of this study confirm the conclusions drawn from infrared examination.

#### Study of Fraction 12 Tar Acids

Fraction 12 was so complex that even the procedure followed for Fraction 6 was not satisfactory. In place of the paper chromatography, gas chromatography was used. A sample of Fraction 12 tar acids was methylated as quantitatively as possible and chromatographed on activated alumina, developing gradiently with ether-pentane mixtures. Then, 10 to 20-microliter samples of selected cuts were gas chromatographed\* and separate cuts were collected. Figure 2 shows the chromatogram and the degree of resolution obtained. Infrared examination of each of the cuts from the gas chromatographic separation showed that indeed a good separation was effected. Most of the cuts were simple mixtures composed of only a few compounds. In fact, Cut 7 was found to be pure 2-methoxynaphthalene. If more reference spectra of methyl ethers of phenols, naphthols, and indanols had been available many more compounds might have been identified.

Table 6 shows a summary of the fractions of tar acids and the information that we can give about them at this time. Upon long standing, Fractions 12, 13, 14, deposited up to 6 per cent of the same solid material. From paper chromatography and infrared study, this solid material appeared to be a pure alkyl-substituted dihydric phenol, such as a substituted hydroquinone.

#### Mass Spectroscopy of Tar Acids in Methanol Solubles

A sample of methanol solubles was supplied to Dr. Irving Wender of the U. S. Bureau of Mines at Bruceton, Pennsylvania. This material was analyzed by mass spectroscopy using a low ionization voltage to suppress all but the major peaks. Table 7 summarizes the spectrogram obtained with relative peak heights at the highest sensitivity. No effort was made to assign quantitative values to the various mass numbers as standards were not run. These data support the evidence obtained in the work just described, and it is evident that a large number of homologues are present for each tar-acid nucleus. The series of tar acids that fit the indenol and acenaphthol families are of interest, as these were not identified in the chromatographic work. Dr. Wender also obtained spectrograms for the trimethyl silyl ethers of the methanol solubles and obtained much the same pattern except the whole series was shifted to higher masses.

\*A modified Recco Distillograph Model D-2000. Research Equipment Corporation, Oakland, California.  
Runs were done at 230 C on a 10-foot column of crushed firebrick coated with Apiezon N grease.

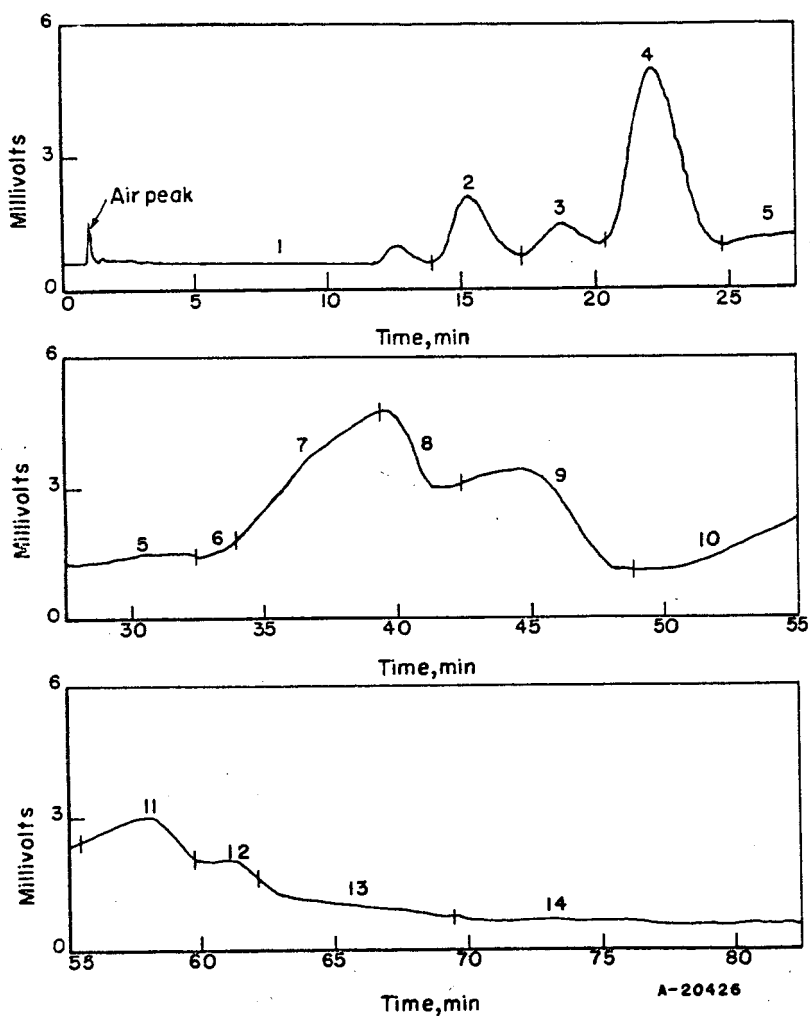

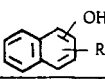

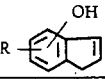
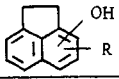



FIGURE 2. GAS CHROMATOGRAM OF CUT 5 FROM CHROMATOGRAPHY OF FRACTION B-12 TAR ACID METHYL ETHERS ON ALUMINA

TABLE 6. SUMMARY OF INFORMATION ABOUT FRACTIONS OF HIGH-BOILING TAR ACIDS

Fraction	Approx. B. P.	Equiv. Wt. of Phenols	Remarks
1	199	116	C <sub>1</sub> -C <sub>2</sub> alkylphenols
2	213	123	C <sub>1</sub> -C <sub>3</sub> alkylphenols
3	223	140	C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub> alkylphenols
4	229	140	C <sub>3</sub> -C <sub>4</sub> alkylphenols; traces of catechols
5	237	129	C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub> alkylphenols; traces of indanols; catechols and/or substituted catechols, 22 per cent
6	245	126	C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub> alkylphenols; indanols; catechols and substituted catechols, about one-fifth of the fraction
7	253	127	Similar to Fraction 6, possibly more indanols and substituted catechols
8	262	117	More substituted catechols; traces of resorcinol
9	269	129	Highly substituted catechols; traces of resorcinols
10	278	131	Similar to 9; about 20 per cent dihydric phenols, some substituted resorcinols; traces of polynuclear phenols
11	286	143	Traces hydroquinone; possibly polynuclear phenols
12	293	146	2 per cent solid material, probably a substituted hydroquinone; no evidence for hydrogenated polynuclear phenols; definitely polynuclear phenols
13	298	153	6 per cent of same solid as 12; polynuclear phenols
14	305	172	4 per cent of same solid as 12; low dihydric content; polynuclear phenols
15	--	157	Dihydric polynuclear phenols or trihydric alkylphenols
16	312	167	Polynuclear phenols
17	318	174	Polynuclear phenols
18	324	175	Polynuclear phenols

TABLE 7. MASS SPECTROGRAPH OF TAR ACIDS IN METHANOL SOLUBLES

Relative Peak Heights for Indicated Tar Acids <sup>(a)</sup>						
R						
H	34	7	9	5.5	1.7	5.0
C <sub>1</sub>	71	17	16	13.8	3.2	4.2
C <sub>2</sub>	60	17.5	18.6	15	3.2	4.1
C <sub>3</sub>	29	3.4	14.1	8.6	2.0	3.1
C <sub>4</sub>	9	2.3	7	3.8		1.7
C <sub>5</sub>	5.2	1.0	2.4	1.4		
C <sub>6</sub>	4.0		1.0	1.2		
C <sub>7</sub>	2.5			1.0		
C <sub>8</sub>	1.0					

(a) Peak heights below a value of 1.0 are not noted.

#### ACKNOWLEDGMENT

In addition to the acknowledgments given in the first paper of this series, the authors wish to thank Josephine Brewer and Clara D. Smith for the infrared studies, C. L. Teitelbaum for the gas-phase chromatography work, Joseph Henry of Union Carbide Corporation for advice on the nonaqueous titration of tar acids, and Irving Wender of the Bureau of Mines for the mass spectrographic data on methanol solubles.

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Not for Publication

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American Chemical Society  
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An Improved Evaluation of Electrode-Binder Pitches  
Using the Compressive Strength of Test Electrodes

by H. L. Jones, Jr.\*, A. W. Simon, and M. H. Wilt  
Mellon Institute, Pittsburgh 13, Pennsylvania

Introduction

One of the major uses for coal-tar pitch is as an electrode binder for Soderberg electrodes in the aluminum industry. The accepted method of determining whether a pitch is of suitable quality for use in production electrodes is to prepare and bake a test electrode using the pitch and a standard calcined petroleum coke, and then to determine the compressive strength and other physical characteristics of the electrode. However, there appears to be very little published in the literature on the methods used for preparing and testing carbon electrodes. One method is described,<sup>1</sup> but it involves the preparation of relatively large electrodes (approximately 6 inches in diameter and 8.5 inches long), which necessitates the use of large and expensive equipment for mixing and baking. An improved modification of this method was developed so that readily available laboratory-size equipment could be used to prepare a batch of four test electrodes, 1.25 inches in diameter and 4 inches long.

This procedure was used in a program to relate various properties of a pitch to its electrode-binder characteristics.

Experimental

Preparation of Test Electrodes

The electrode paste which is made from a mixture of the pitch and petroleum coke particles (see Table I) is baked in a graphite mold. The molds are prepared from graphite rods 1-5/8 inches in diameter (National Carbon Company, Type AGX or AJX) which are cut into pieces 5 inches long. A hole 1-1/4 inches in diameter is drilled throughout the length of each piece. The drilled hole is reamed with a tapered reamer so that the inside diameter of the one end is 1-9/32 inches and the other end is 1-1/4 inches. This taper permits easier removal of the electrode after baking. The inside of the mold is then lined by gluing in a layer of Kraft wrapping paper. A template is then used to aid in drilling 96 vent holes 0.076 inches in diameter (#48 drill) through the graphite shell of the mold (see Figure 1). If desired, the molds can be reused several times by cleaning, relining, and punching vent holes in the liner.

The pitch is broken into small pieces and placed into a steam-jacketed, one-quart sigma blade mixer (Charles Ross and Son) where it is melted at a temperature of about 130°C. For pitches with a softening point of about 90°C, ten minutes is usually sufficient. The mixer blades are placed into motion, and the previously heated (120-130°C) petroleum coke particles are added starting with the coarsest fraction and allowing five minutes of mixing between the addition of fractions. After the last fraction is added, the paste is mixed for five minutes.

\* Present Address: Atlas Powder Company, Wilmington, Delaware

Table I

Composition of Paste Used in Preparing Test Electrodes

<u>Component</u>	<u>Weight, g</u>	<u>Weight Per Cent</u>
Pitch	262.8	31.1
Calcined Petroleum Coke		
10 to 30 Mesh*	116.7	13.8
30 to 50 Mesh	93.4	11.0
50 to 100 Mesh	110.0	13.1
100 to 200 Mesh	75.9	9.0
200 to 325 Mesh	58.4	6.9
325 to Pan	<u>128.2</u>	<u>15.1</u>
Total	846.3	100.0

\* U. S. Standard Sieve Sizes

While the paste is being mixed, four of the graphite molds are heated to about 120°C using an electrical beaker mantle in which the molds rest on a flat graphite plate. The molds are gradually filled in turn with small portions of paste taken directly from the mixer using a metal rod as a tamper to achieve a uniform density. The paste behaves as a heavy fluid after it has been evenly packed in the mold. Each mold is filled to within one-half inch of the top.

The filled molds are then allowed to cool and the paste forms a hard solid. Two grams of petroleum coke particles, 200 to 325 mesh, are placed on top of the solidified paste. The four molds are placed in a holder (Figures 2 and 3) which is used during the baking. Nine-pound steel weights are placed on top of the paste to simulate somewhat crudely the weight of the unbaked paste above the Soderberg electrode in an actual furnace. The weights are kept in place and guided by the top of the mold holder.

Description of Baking Apparatus

A schematic diagram of the entire baking assembly is given in Figure 4. The electrodes are baked in a specially designed retort fabricated from type 310 stainless steel (Figure 5). Openings are provided for a chromel-alumel thermocouple, the nitrogen purge gas, and an exit tube for the vapors carried out by the gas. The exit tube is wrapped with nichrome heating wire to prevent the pitch vapors from condensing. The furnace used is a Hevi Duty Model 506 electrical crucible furnace with an opening 5 inches in diameter and 9 inches deep. A Brown Instrument Company cam-type program controller is used to control the baking cycle over the range from 25 to 1000°C. Due to the slow response of the thermocouple inside the retort, a second thermocouple placed near the furnace heating element is used as the controlling point. Controller cams were prepared by trial and error in order to obtain the proper temperature program as measured by the thermocouple inside the retort.

Baking of the Electrodes

The holder containing the molds is placed in the retort, and the top is bolted on using a metallic gasket to obtain an airtight seal. Nitrogen which has been passed over copper gauze at 600-650°C to remove traces of oxygen is used as an inert atmosphere to prevent oxidation inside the retort during baking and cooling. The electrodes are baked according to the schedule given in Table II. After the

retort has cooled to 150°C, the molds containing the baked test electrodes are removed. The electrodes are carefully removed from the molds by pressing them out with the aid of a hydraulic press.

Table II

Baking Schedule for Test Electrodes

<u>Temperature, C</u>	<u>Time, Hours</u>
25-200	2.0
200-500	12.0
500-1000	8.5
Soak at 1000	<u>1.0</u>
Total	23.5

Electrical Resistivity of the Electrode

The test specimen is prepared for the electrical resistivity measurement by facing off each end on a lathe so that the ends are parallel and the distance between them is 3-1/8 inches. The resistivity is then measured with the apparatus shown in Figure 6. The specimen is firmly secured between the brass plates. The fixed brass points (3.0 inches apart) to which the potentiometer leads are attached are placed against the electrode and held firmly in place by a 1000 g weight. A known current is passed through the electrode by closing the circuit, and the potential drop is measured with the potentiometer. Four readings, 90 degrees apart, are taken around the circumference of the electrode and averaged. The resistivity is then calculated from the following formula:

$$\rho = \text{resistivity (ohm-cm)} = \frac{EA}{IL}$$

where E (volts) is the potential drop, A (sq cm) is the area of the end of the electrode, I (amp) is the current in the system, and L (cm) is the distance between the contact points.

Apparent Density

The apparent density of the test specimen of the electrode in grams per cc is determined directly by dividing the weight (in grams) by the total volume (in cc's).

Compressive Strength

Each specimen is then cut on a band saw to obtain two pieces, which after grinding on a surface grinder in a special holder (Figure 7) to obtain parallel ends, yield pieces 1.25 inches in height.

The compressive strength of each piece is determined on a compression-testing machine (Tinius-Olsen Company) using a ram speed of 0.05 inches per minute. The results of all the determinations (usually 6 to 8) are then averaged.

Results and Discussion

The preliminary work on developing the method was based on the use of a 46-hour baking cycle. In order to shorten the amount of time involved in obtaining results, baking cycles of 15 and 23.5 hours were tried. The results obtained for

four different pitches are given in Table III. The data indicate that over the range studied the length of the baking cycle does not have a significant effect on the compressive strength. However, with the 15-hour cycle, the electrodes showed a tendency to develop cracks on the surface. Because of this, the 23.5-hour schedule was adopted as the standard baking period.

Table III  
Effect of Length of Baking Cycle on the  
Compressive Strength of the Electrode

<u>Pitch*</u>	<u>Compressive Strength, kg/sq cm</u>		
	<u>15-Hour</u>	<u>23.5-Hour</u>	<u>46-Hour</u>
L	487	470	481
B	--	295	281
E	--	297	295
H	--	319	335

\* See Table IV for pitch properties.

Table IV  
Properties of Pitches Used for Preparing Test Electrodes

<u>Pitch Sample</u>	<u>Softening Point, C</u> <u>Cube-in-Air<sup>2</sup></u>	<u>Benzene Insoluble, Wt %<sup>3</sup></u>	<u>Coking Value, Wt %<sup>4</sup></u>	<u>Carbon: Hydrogen Ratio</u>	<u>Characterization Factor No. 1*</u>	<u>Compressive Strength, kg/sq cm</u>
A	86.0	26.2	53.4	1.82	97.2	463
B	88.2	13.0	49.8	1.60	79.7	357
C	88.6	31.7	53.5	1.71	91.5	426
D	89.0	33.2	58.6	1.80	105.5	549
E	89.2	20.2	51.9	1.64	85.1	394
F	90.2	32.6	57.1	1.93	110.2	577
G	90.6	17.5	50.2	1.78	89.4	461
H	91.1	21.2	50.1	1.75	87.7	424
I	93.5	29.7	54.1	1.87	101.2	492
J	94.9	28.0	52.7	1.76	92.8	541
K	103.0	30.8	56.4	1.83	103.2	495
L	106.3	27.9	59.5	1.79	106.5	470

\* Coking value multiplied by the atomic carbon:hydrogen ratio.

Compressive strength determinations, electrical resistivities, and apparent densities for a typical batch of test electrodes are given in Table V. Although the compressive strength determinations within a batch show a somewhat high deviation, the fact that the final compressive strength value is the average of 6 to 8 results gives reproducible results between batches. This is demonstrated in Table VI, where duplicate determinations are given for five different pitches.

Table V

Characteristics of Electrodes Produced from Pitch G

<u>Whole Electrode</u>			<u>Electrode Sections</u>	
<u>Electrode No.</u>	<u>Apparent Density, g/cc</u>	<u>Resistivity, ohm-cm</u>	<u>Section</u>	<u>Compressive Strength, kg/sq cm</u>
1	1.43	0.0064	Top	501
			Bottom	455
2	1.41	0.0066	Top	412
			Bottom	445
3	1.40	0.0071	Top	428
			Bottom	458
4	1.42	0.0066	Top	--*
			Bottom	477
Average	1.42	0.0067		454

\* Not tested.

Table VI

Reproducibility Between Electrode Batches

<u>Pitch</u>	<u>Compressive Strength, kg/sq cm</u>	
	<u>Batch #1</u>	<u>Batch #2</u>
C	429	422
D	557	541
E	380	408
G	468	454
I	512	472

It has been reported<sup>5)</sup> that a correlation existed between the compressive strength of a test electrode and the product of the coking value and atomic carbon to hydrogen ratio (characterization factor 1). This factor has been calculated for the pitches used in the present study (Table IV) and has been plotted against compressive strength (Figure 8). The standard deviation about the curve was calculated to be 26 kg/sq cm or 5.5 per cent of the mean of the range of compressive strengths observed. The data of Charette and Bischofberger indicate that their deviation was 19 kg/sq cm or 6.2 per cent of the mean for the range of compressive strengths that they studied.

Summary

In order to evaluate coal-tar pitches for use as electrode binders in carbon electrodes, a method for preparing test electrodes and measuring their compressive strengths was developed. The procedure uses laboratory-size equipment and requires less than 300 g of pitch sample to produce a batch of four electrodes. In addition to compressive strengths, the apparent densities and electrical resistivities of the electrodes are determined. The developed procedure has proved useful in ascertaining the binder quality of a wide variety of coal-tar pitches.

Acknowledgment

This work was carried out by the Coal Chemicals Project sustained by the United States Steel Corporation, to whom the authors are grateful for permission to publish these results.

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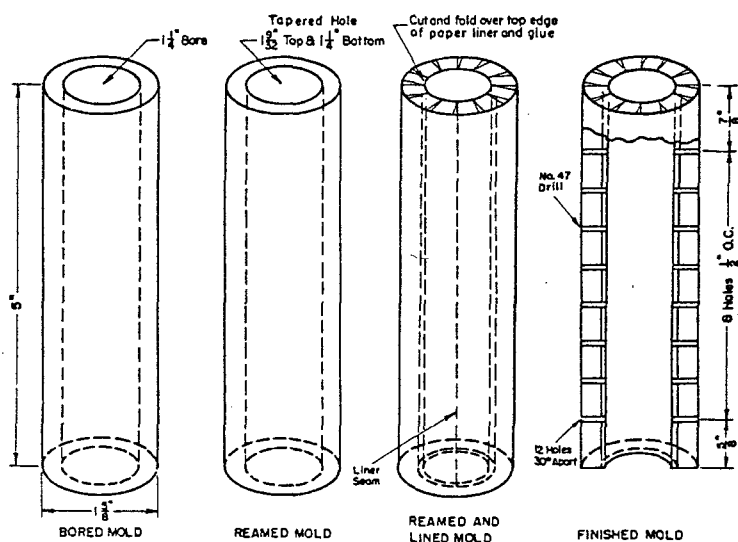


Figure 1. Various Stages in the Preparation of a Graphite Mold

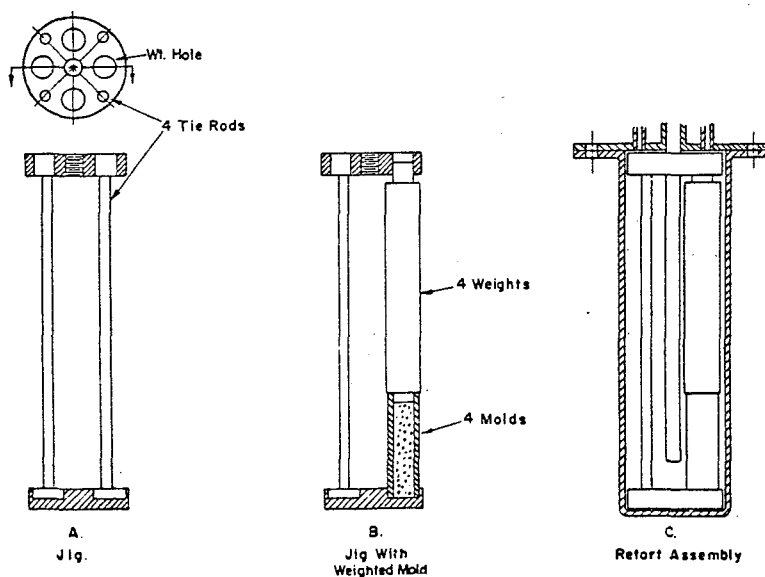


Figure 2. Loading of Filled Molds in Holder and Retort

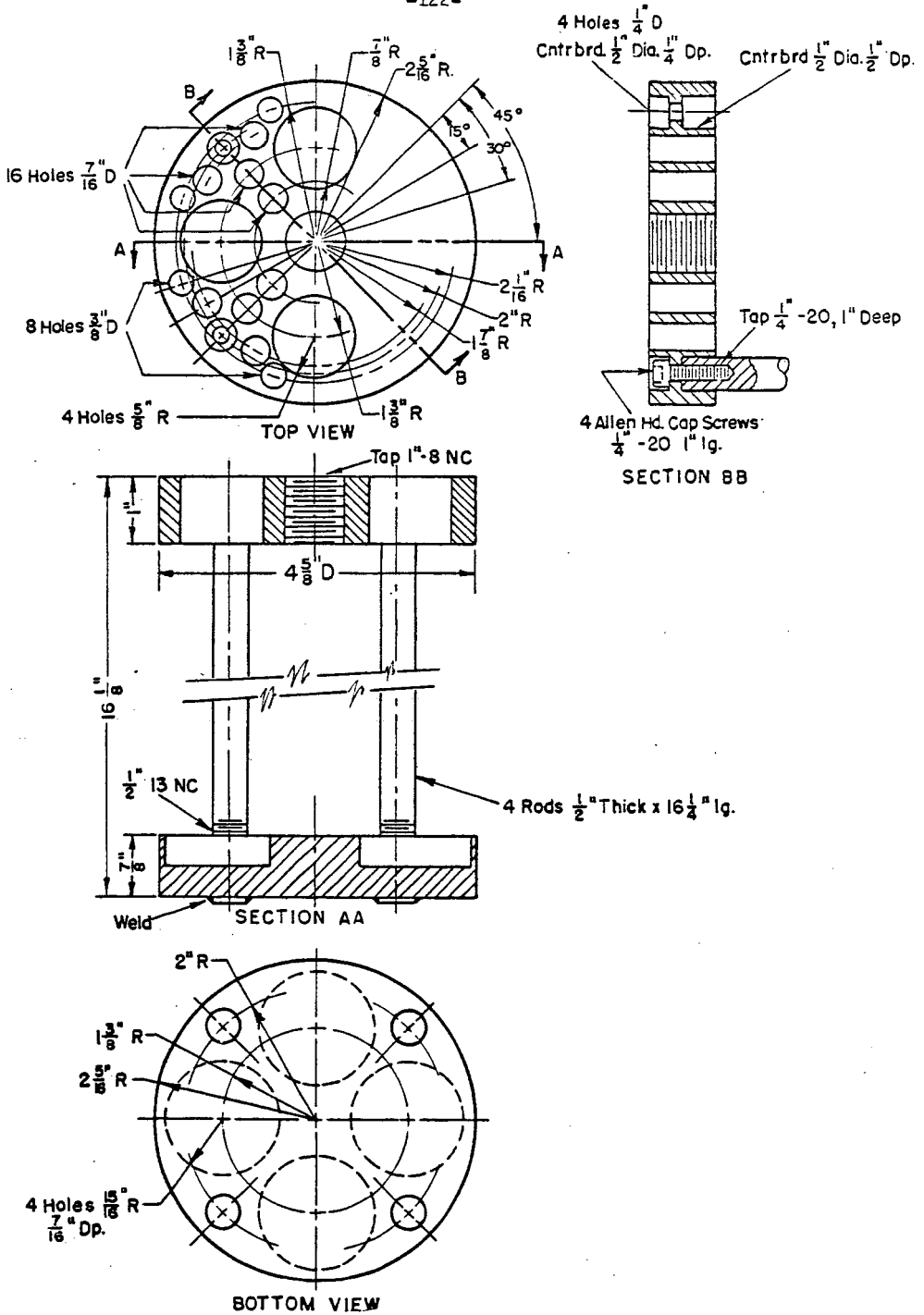


Figure 3. Construction Details of Mold Holder and Weight Guide

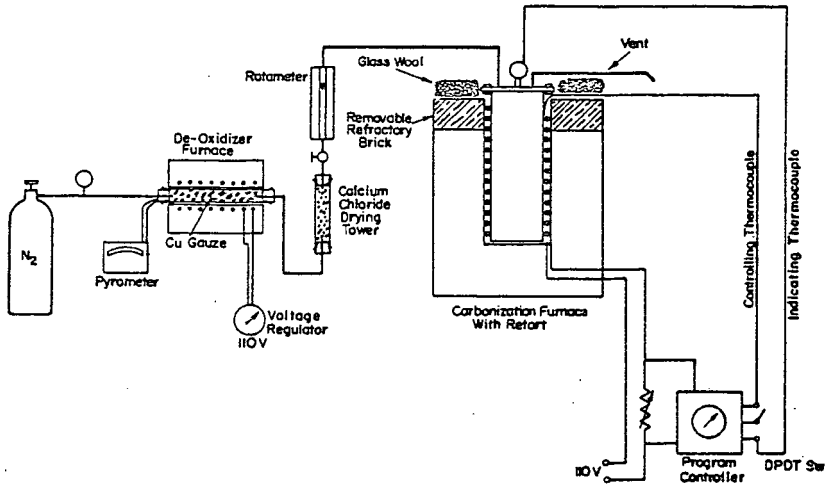


Figure 4. Schematic Diagram of Apparatus for Baking Test Electrodes

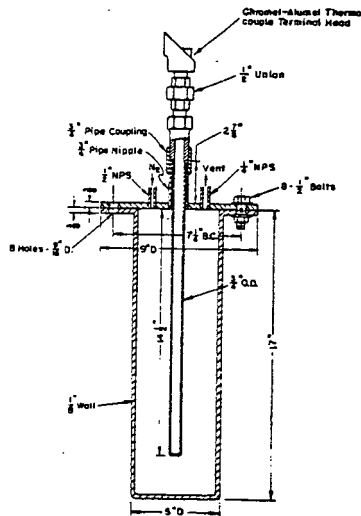


Figure 5. Retort for Baking Test Electrodes

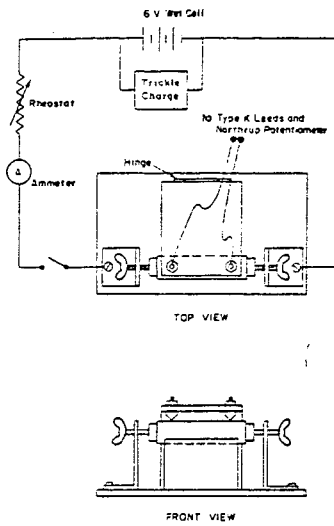


Figure 6. Apparatus for Measuring Electrical Resistivity

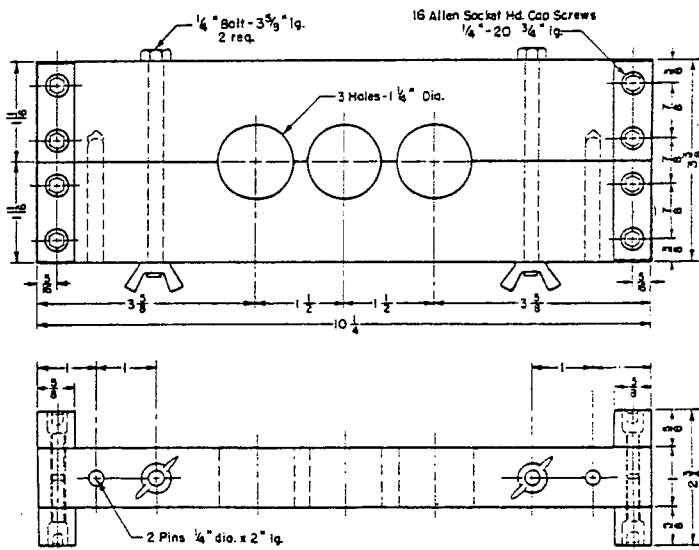


Figure 7. Holder for Grinding Ends of Test Specimens for Compressive-Strength Determinations

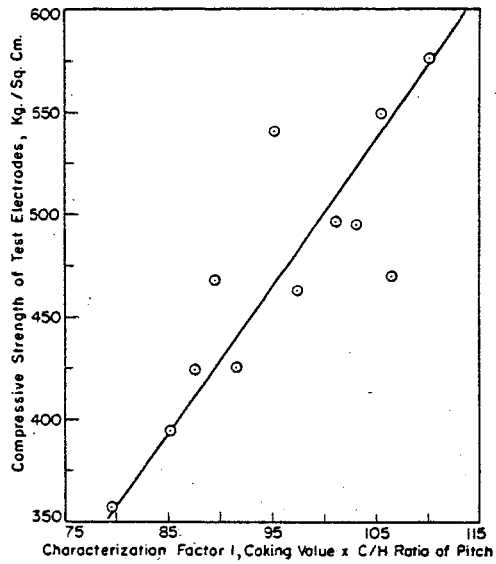


Figure 8. Relationship Between Compressive Strength of Test Electrode and Characterization Factor No. 1 of the Pitch

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The Surface Properties of the  
Quinoline-Insoluble Fraction of Pitch

by M. S. Morgan, W. H. Schlag, and M. H. Wilt  
Mellon Institute, Pittsburgh 13, Pennsylvania

Introduction

The general consensus of the literature on binder materials for the production of Soderberg electrodes in the aluminum industry is that a coal-tar pitch is the preferred binder material.<sup>1)</sup> Studies directed toward establishing the most suitable methods for the preparation of an electrode-binder pitch from a coal tar and methods for improving the binding quality of pitches have been of considerable interest to both the producer and the consumer of electrode-binder pitch. Although compressive-strength measurement on test electrodes has been a satisfactory method of evaluating pitches for production of carbon electrodes, this method is time-consuming. It would be much more satisfactory to be able to predict electrode-binder efficacy on the basis of the chemical and physical properties of the pitch. Only then would it be possible to interpret the binding action in terms of pitch composition and perhaps to modify the pitch in a manner which would have a predictable effect on the binder action.

Charette and Bischofberger<sup>2)</sup> concluded that pitch quality, as expressed by the compressive strength of test electrodes, is apparently not a function of any pitch property taken individually, but rather of a combination of properties. These investigators and others have considered correlations of compressive strength of electrodes with such properties of pitch as coking value, density, aromaticity, softening points, and distribution of fractions produced by solvent extraction.

One general method of characterizing pitches is that of solvent analysis. In one such technique, the pitch is extracted first with a paraffinic solvent and the residue is then re-extracted successively with benzene and quinoline. Martin and Nelson<sup>3)</sup> state that "in pitch binder quality, the quinoline-insoluble (Q.I.) fraction, essentially a nonfusible powder, is important".

The technological importance of the Q.I. fraction of pitch is recognized by the inclusion of a Q.I. minimum in many specifications for electrode-binder pitches. Information on the scientific significance of the Q.I. material is rather scarce. It is known that the Q.I. material per se does not contribute directly to the binding action of the pitch,<sup>4)</sup> and generally it is considered as inert material which may have a beneficial effect in decreasing the effect of temperature on the viscosity of pitch.<sup>5)</sup> Thus, one notes in the literature a tendency to consider the Q.I. portion of pitch as a finely dispersed carbonaceous filler of questionable function in the binding action of the pitch.

Because little information could be found on the surface properties of the Q.I. fraction of pitch and because studies of the surface chemistry of carbon black have led to a better understanding of the use of this material in the rubber industry, an exploratory study of the surface properties of the Q.I. portion of pitch was made. It was hoped that this information might lead to a better understanding of the function of Q.I. material in the applications of pitch as an electrode binder.

### Experimental

For this work, a total of nine experimental binder pitches, representing a considerable range of Q.I. content, was selected. The usual analytical data on these pitches are summarized in Table I. Pitches 1 through 6, representing a range of Q.I. from 2.44 to 13.1 per cent, had been prepared to an approximate constant softening point of 90°C. In order to achieve rather extreme variation in Q.I. content, pitch A was thermally treated to produce pitch B having a very high benzene-insoluble and quinoline-insoluble content. Pitch C was produced to have a low Q.I. content by centrifugation of a quinoline suspension of the parent tar of pitch A, followed by removal of the quinoline and further distillation.

Table I

#### Analytical Data on Experimental Pitches

Pitch	Softening Point, °C C.I.A.*	Benzene Insoluble, Wt %	Quinoline Insoluble, Wt %	Beta- Resin**	Coking Value, Wt %	Carbon, %	Hydrogen, %	Atomic C/H Ratio
1	89.0	33.2	13.1	20.1	56.8	93.34	4.36	1.80
2	90.2	32.6	12.8	19.8	57.1	93.41	4.07	1.93
3	93.5	29.7	10.58	19.1	54.1	93.31	4.18	1.87
4	94.9	28.0	9.13	18.9	52.7	92.88	4.44	1.76
5	90.6	17.5	6.87	10.6	50.2	92.55	4.38	1.78
6	88.2	13.0	2.44	10.6	49.8	91.35	4.77	1.61
A	102.3	25.5	12.4	13.1	56.7	93.22	4.24	1.84
B	98.5	50.3	35.0	15.3	64.9	93.48	4.00	1.96
C	95.0	25.0	4.2	20.8	51.9	93.29	4.52	1.73

\* Cube-in-Air Method.

\*\* Benzene Insoluble Minus Q.I. Equals Beta-Resin.

- 1 Thermal Treatment of a 74°C pitch at 380°C for 24 hours and back-blending with 9.1 per cent of starting pitch.
- 2 Laboratory distillation of soft pitch from a production tar.
- 3 Laboratory distillation of 36.2 weight per cent from a production tar.
- 4 Blend of 88.55 weight per cent 105°C pitch (produced by distillation of light tar at 50 mm to 300°C) with 11.45 per cent of coal-tar distillate oil (boiling 230-270°C).
- 5 A production pitch after removal of n-heptane solubles.
- 6 Laboratory distillation of a 69°C pitch from light tar.
- A A pitch produced by plant distillation of production tar.
- B A pitch produced by thermal treatment of pitch A to have maximum benzene-insoluble and quinoline-insoluble content.
- C A pitch produced by adding quinoline to the parent tar of pitch A, centrifuging this mixture to remove insolubles, and then distilling.

The Q.I. fractions used for the present study were isolated as follows:  
A 100 g portion of pitch was crushed and ground to pass a 60-mesh sieve. The pitch was then added slowly with stirring to 250 ml of warm (70-90°C) quinoline in a 600 ml beaker. After 15-20 minutes at this temperature, the mixture was filtered through a

Buchner funnel fitted with a Whatman No. 50 filter paper. The retained Q.I. were washed with an additional 250 ml of warm quinoline in small portions and then with 500 ml of benzene to remove the quinoline. After air drying, the Q.I. were oven-dried at 110-115°C for one hour. This method of preparation gave yields of Q.I. materials nearly equal to those obtained by the analytical procedure and reported in Table I.

Surface-area measurements were made using the method of Brunauer, Emmett, and Teller.<sup>6)</sup> The samples were degassed at 200°C for 12 hours before measuring the nitrogen isotherm at 77°K.

Specimen electrodes were prepared using the various pitches as binders according to the procedure of Jones, Simon, and Wilt.<sup>7)</sup>

### Results and Discussion

The data on the Q.I. fractions of the experimental pitches are summarized in Table II. For these particular samples, it was noted that the surface area per gram of Q.I. tends to decrease as the amount of Q.I. in the pitch increases (Figure 1). This trend is exhibited both by pitches 1 through 6 and by the interrelated series, A, B, C, although the rate of change varies. This observation suggests that a process such as thermal treatment, which tends to increase the amount of Q.I. in the pitch, also produces an agglomeration or increase in particle size of the Q.I. material.

Table II

#### Data on the Quinoline Insolubles

Quinoline- Insoluble Fraction	C.V. - Q.I. Q.I.	Surface Area, m <sup>2</sup> /g	Surface Area per 100 g Pitch, m <sup>2</sup>	Carbon, %	Hydrogen, %	Atomic C/H Ratio
1	3.34	9.4	123	92.59	3.06	2.54
2	3.46	10.4	133	93.02	2.43	3.21
3	4.1	13.2	140	93.06	2.01	3.89
4	4.8	16.3	148	91.60	2.11	3.64
5	6.28	16.8	116	93.13	2.00	3.90
6	19.4	22.9	55	91.45	2.47	3.10
A	3.57	15.9	197	94.76	1.89	4.21
B	0.85	8.0	280	94.67	3.04	2.61
C	11.4	19.4	82	93.36	2.30	3.41

It is of interest to note that thermal treatment of a pitch (A) containing 12.4 per cent Q.I. with a surface of 15.9 m<sup>2</sup>/g yielded a product pitch (B) containing 35.0 per cent Q.I., but with a surface of only 8.0 m<sup>2</sup>/g. When the Q.I. content was reduced to 4.2 per cent by extraction of the parent tar with quinoline, centrifugation to remove most of the Q.I., removal of solvent, and distillation, the residual Q.I. in the pitch (C) had a surface area of 19.4 m<sup>2</sup>/g.

In a number of cases (such as the Q.I. from pitches 6 and 2), the Q.I. was found to be almost entirely spherical in habit (Figures 2 and 3). It will be noted that the particle sizes are of the same order of magnitude as those anticipated from surface area measurements, with pitch 6 having the smaller particle size and higher surface area.

Having shown that Q.I. material can differ in surface area and particle size, it was of interest to examine the surface for differences in chemical reactivity. For this purpose, the polarographic reducibility of the surface of the Q.I. material was determined by the method of Hallum and Drushel.<sup>8)</sup> As noted in Figure 4, the polarographic reducibility of the Q.I. appeared to be a direct function of the surface

area. This relationship between polarographic reducibility and surface area was taken as an indication of the chemical uniformity of the surface of the Q.I. material. The limited number of samples examined prohibit any firm position on this indication. However, the significance of surface reducibility might be more profitably pursued in the study of Q.I.'s of the same surface area where differences in reactivity are suspected. A sample of petroleum coke of comparable surface area showed no reducibility.

Before considering the effect of the surface area of the Q.I. portion of pitches on the properties of electrodes prepared from pitches, the available data were examined for evidence of surface effects during the coking of the pitch itself. If the surface area of the Q.I. is an important factor in binding action, it seemed reasonable to anticipate some effect on the yield of coke available from the pitch.

If it is assumed that all quinoline-soluble material is available for the formation of coke and that Q.I. is relatively unchanged during coking, a plot of coke formed (coking value - Q.I.) per unit weight of Q.I. versus the surface area per unit weight of Q.I. should give an indication of the effect of Q.I. surface area on the yield of coke. Figure 5 shows this relationship and indicates that Q.I.'s with a high surface area promote a high yield of coke per unit weight of Q.I. The variant pitches B and C, produced from A, show this same qualitative relationship. This relationship suggests that the surface of the Q.I. may function as the site of coke formation.

The usual test data for the specimen electrodes are tabulated in Table III. The apparent density, resistivity, and compressive strength of the electrodes as a function of the amount of surface available from the Q.I. in 100 g of binder are shown in Figures 6, 7, and 8. These figures show that apparent density and compressive strength reach a maximum at about 125-150 m<sup>2</sup> of surface in 100 g of pitch, and the resistivity reaches a minimum in the same region.

Table III  
Test Data on Specimen Electrodes  
Prepared from Experimental Pitches

<u>Pitch</u>	<u>Apparent Density,</u> <u>g/cm<sup>3</sup></u>	<u>Resistivity,</u> <u>ohm-cm</u>	<u>Compressive Strength,</u> <u>kg/cm<sup>2</sup></u>
1	1.46	60.1 x 10 <sup>-4</sup>	557
2	1.47	60.3 "	577
3	1.44	65.2 "	472
4	1.45	59.0 "	541
5	1.43	66.8 "	468
6	1.39	70.1 "	357
A	1.45	59.6 "	490
B	1.36	74.0 "	356
C	1.46	55.5 "	538

Also, these figures suggest that an optimum surface area or particle size of Q.I. exists which permits the formation of electrodes with optimum properties. The results are quite similar to those of Krylov, et al, who found in their studies of the free-carbon content of pitch that at about 16 per cent free carbon the density and compressive strength of electrodes pass through a maximum and resistivity reaches a minimum.<sup>9)</sup>

#### Conclusions

Although the Q.I. fraction of an electrode-binder pitch reportedly has no binding action in itself, it is credited with being important to electrode-binder

efficacy of the pitch. The actual role of the Q.I., however, remains vague. It was therefore the purpose of this study to examine the surface properties of Q.I.'s of several experimental pitches in the hope that some information might thus be obtained which would be helpful in elucidating the role of the Q.I. On the basis of nine different pitches, the Q.I.'s of which varied, irregularly, from 2.44 to 35 per cent, the following effects were observed:

1. The larger the percentage of Q.I. content of a pitch, the smaller is the surface area per gram of Q.I., and hence the larger is the average particle size. This is qualitatively borne out by electron photomicroscopy.
2. The polarographic reducibility of the Q.I. appears to be directly related to surface area, an indication that the reactivity of the surface is essentially uniform.
3. The yield of new coking value per gram of Q.I.,  $\frac{C.V. - Q.I.}{Q.I.}$ , is directly related to the surface area per gram of Q.I. This suggests that the Q.I. surface may serve as the site of new coke formation.
4. Evaluation of test electrodes prepared from these pitches indicates that there may be an optimum range of interfacial area between the Q.I. and the remainder of the pitch. In this range, the apparent density and compressive strength of the electrodes pass through a maximum and the resistivity through a minimum.

This study has been an examination of some of the parameters of the Q.I. which might shed light on its function in the pitch. It is hoped that these preliminary, generalized trends of some Q.I. properties will be useful to investigators who are currently exploring this field.

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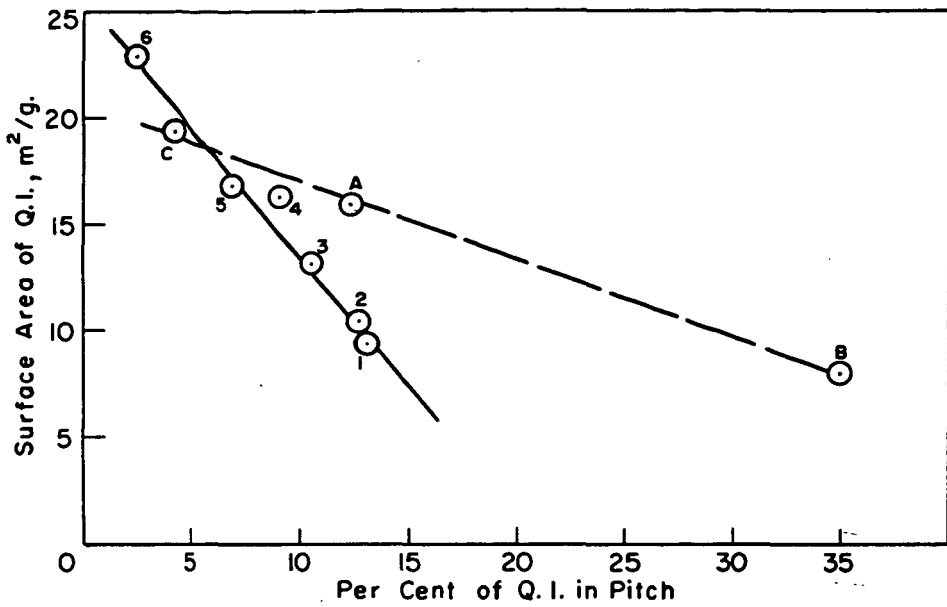


Figure 1. The Q.I. Content of the Pitch Versus Q.I. Surface Area

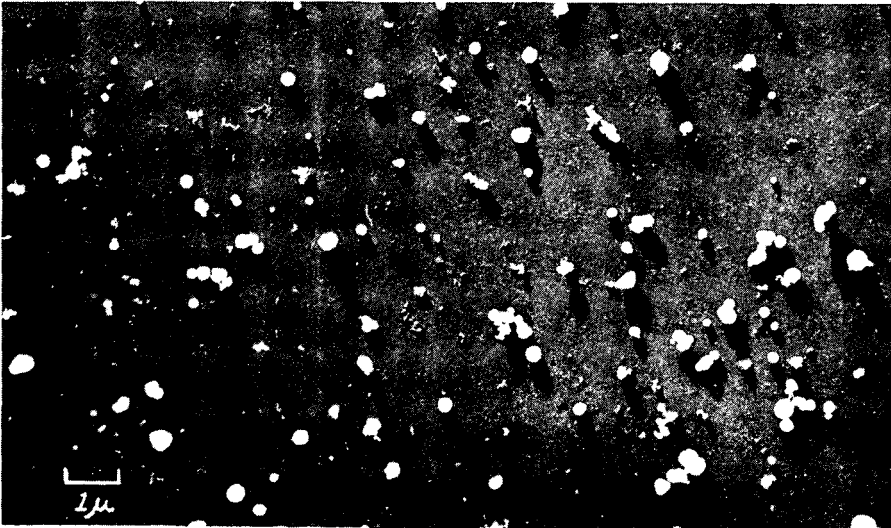


Figure 2. Photomicrograph of the Q.I. of Pitch 6, Illustrating a Q.I. of High Surface Area



Figure 3. Photomicrograph of the Q.I. of Pitch 2, Illustrating a Q.I. of Low Surface Area

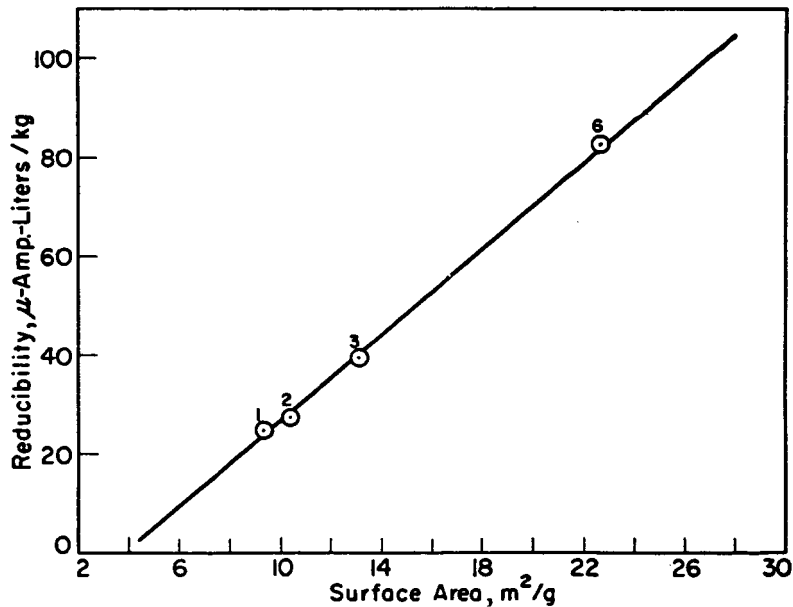


Figure 4. Relationship of the Polarographic Reducibility to the Surface Area of the Q.I.

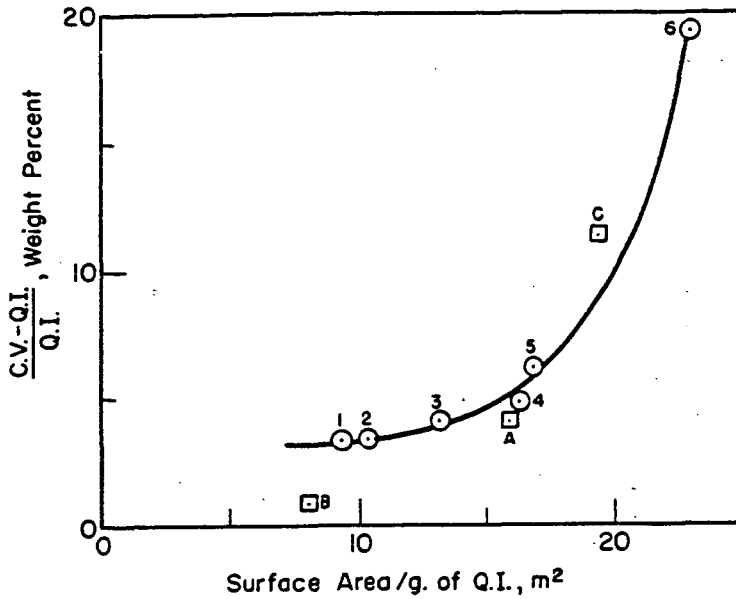


Figure 5. Relationship Between the Yield of New Coking Value per Gram of Q.I. (C.V. - Q.I./Q.I.) and the Surface Area per Gram of the Q.I.

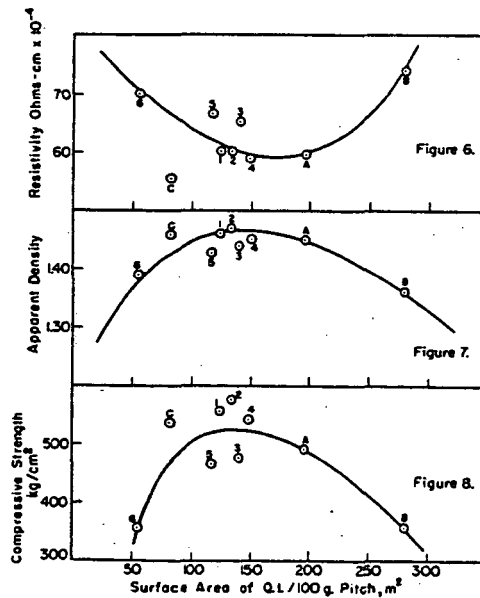


Figure 6, 7, & 8. Relationships Between the Resistivity, Apparent Density, and Compressive Strength of Test Electrodes Prepared from Each of the Experimental Pitches and the Surface Area of the Q.I. in 100 g of the Respective Pitch

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X-RAY ANALYSIS OF ELECTRODE BINDER PITCHES AND THEIR COKES

Sidney S. Pollack and Leroy E. Alexander  
Mellon Institute, Pittsburgh 13, Pa.

INTRODUCTION

The highly aromatic character of electrode binder pitches permits them to be studied by the same x-ray methods which have previously been applied to carbon blacks (1). The wide-angle x-ray scattering patterns are similar (see Figure 1) and show that both substances are built up of pseudocrystallites, or parallel-layer groups (to be referred to in this paper as crystallites), composed of graphite-like layers together with varying amounts of disorganized material. The quinoline soluble and insoluble fractions and the cokes of these pitches are also found to have a similar fine structure (Figure 1). All these materials, then, are composed principally of graphite-like layers, some of which are arranged turbostratically (2) in crystallites and some of which are unassociated. In the ensuing discussion we shall denote by  $\underline{D}$  the fraction of disorganized material, by  $\underline{L}_a$  and  $\underline{L}_c$  the dimensions of the crystallites respectively parallel and normal to the constituent layers, by  $\underline{d}_M$  the interlayer spacing, by  $\underline{M}_e$  the effective number of layers in the crystallite, and by  $\underline{f}_1, \underline{f}_2, \underline{f}_3$ , etc., the weight fractions of graphite-like layers respectively unassociated, associated in groups of two, associated in groups of three, etc.

The degree of physical heterogeneity of a specimen, whether it be due to the presence of particles, pores in solid matter, or discrete regions differing in density, is revealed by x-ray scattering at small angles. In favorable cases something can be learned about the shape and size distribution of the particles, or other entities, producing the scattering. In the present investigation we have employed the theory of x-ray scattering by dense systems which was developed by Kratky (13), Porod (16), and coworkers (9).

For clarity the wide-angle x-ray study will be presented first. This part of the paper will include a description of improvements in the experimental technique that have been adopted since the earlier report (1) and numerical results for fourteen samples, comprising six pitches and their 575° C. cokes and a beta resin and its 575° C. coke. The second part of the paper will deal with the small-angle scattering investigation of three pitches, their quinoline soluble and insoluble fractions, the 575° C. cokes of the pitches, and a beta resin. Finally some general conclusions will be drawn concerning the structure of electrode binder pitches and their cokes in the light of both the wide- and small-angle x-ray findings.

WIDE-ANGLE X-RAY ANALYSIS

Improvements in Experimental Procedure. Except for certain improvements to be described herewith, the counter diffractometric technique employed was the same as that described previously (1). As explained by Milberg (15), in studying specimens which are weakly absorbing to x-rays by the reflection technique, it is possible to make systematic errors in measuring intensities if the receiving slit is too narrow to permit the detector to "see" the entire irradiated volume of the sample. In the present study such errors were eliminated by removing the scatter slit of the Norelco goniometer. In Milberg's notation this means making  $\underline{a}$  large with respect to  $\underline{A}$ . Furthermore, the specimen dimensions were increased somewhat to permit intensities to be measured

over the angular range  $2\theta = 12^\circ$  to  $144^\circ$ . The sample dimensions were 31 mm. long x 11 mm. wide x 8 mm. deep when used with a  $1^\circ$  divergence slit and 0.006-inch receiving slit.

$\text{CuK}\alpha$  radiation of rather high monochromatic character was obtained by using Ross balanced filters of nickel and cobalt (11,17). Satisfactory thicknesses were realized by varying them until both filters gave the same transmitted intensity at the wavelength of  $\text{CuK}\beta$ , 1.392 Å., while the Ni filter absorbed approximately 50% of  $\text{CuK}\alpha$ , 1.542 Å. The experimental counting rates were corrected for resolving time losses of the Geiger counter and for polarization in the usual way (1). Normalization of this corrected experimental curve (A in the notation of reference (1)) to electron units was accomplished by fitting it to the independent scattering curve (B) of carbon at the angle  $(\sin \theta)/\lambda = 0.505$ , a method suggested to one of the authors by P. B. Hirsch in a private communication. This method is justifiable on the basis of calculations by R. Diamond (4) of the x-ray scattering by discrete graphitic, or aromatic, layers of various sizes which demonstrate that the diffracted intensity is nearly independent of the layer dimension at this angle. As in the previous work the carbon scattering factors of McWeeny (14) were used; however, the values of the incoherent scattering computed by Keating and Vineyard (10) were employed rather than the earlier data tabulated by Compton and Allison.

In contrast to the previous investigation (1) the present study has made use of the (11) rather than (10) line in deducing the mean layer diameter  $L_a$  of the crystallites. There are two reasons for this change in choice of (hk) reflection. First, the reliability of the independent scattering curve of carbon is undoubtedly greater at the larger angle involved ( $s = 0.84$  rather than  $0.49$ , where  $s = 2(\sin \theta)/\lambda$ ). Second, as noted by Diamond (4), the (hk) scattering function is less perturbed at this higher angle by the (00L) interference function since the amplitudes of its maxima decay rapidly with increasing order, becoming negligible as a general rule for  $L > 4$ . In this connection it may be mentioned that experience in this laboratory indicates that values of  $L_a$  derived from the (10) line tend to be larger than those derived from the (11) line, although this does not invariably hold.

#### INTERPRETATIVE PROCEDURE AND RESULTS

The several structural parameters,  $D$ ,  $L_a$ ,  $L_c$ ,  $d_M$ ,  $M_a$ , and the fractions  $f_1$ ,  $f_2$ ,  $f_3$ , etc., have been calculated from the experimental intensity curves in much the same way as was done in the last study. (1) As before, the (002) line profile has been converted to the symmetrical form  $I'$  by means of the proper choice of  $D$  in the equation

$$I' = \frac{s^2}{0.0606} \times \frac{I - D}{1 - D} \quad (1)$$

This choice of  $D$  can be made directly if equation (1) is first converted to the form

$$D = \frac{s_2^2 I_2 - s_1^2 I_1}{s_2^2 - s_1^2} \quad (2)$$

wherein  $I_1$  and  $I_2$  are the experimental intensities at two points  $s_1$  and  $s_2$  equidistant from the point of maximum intensity and close to the minima that lie on either side of the (002) maximum. For example, the angles  $s_1 = 0.16$  and  $s_2 = 0.40$  may be used if the maximum point falls very close to  $0.28$ .

The  $L_a$  dimension of the crystallites has been computed in two ways (Table I): first, by using the Warren equation for the height of an (hk) profile as applied by Franklin (6) (see reference (1), equations (5) and (6)); second, from the width of the (11) profile at half-maximum intensity using the Scherrer crystallite size

formula with an appropriate value of the shape factor,  $K = 1.84$ , (12,19)

$$L_a = \frac{1.84 \lambda}{w \cos \theta} \quad (3)$$

Both these methods of calculating  $L_a$  make the implicit assumption that any given specimen contains crystallites with a single uniform  $L_a$  dimension. Obviously this is not as realistic as a distribution of  $L_a$  values. Diamond (5) has recently described a least-squares method for selecting the most probable distribution of  $L_a$ 's from the shape of an  $(hk)$  profile. Also the  $L_c$  dimension has been computed in two ways: first, through the use of the effective number of layers,  $M_e$ , which makes allowance for the distribution of  $M$  values; second, from the width of the (002) band at half-maximum intensity by means of the Scherrer crystallite size formula

$$L_c = \frac{0.9 \lambda}{w \cos \theta} \quad (4)$$

in which the shape factor is set equal to 0.9. The second method does not take account of the distribution of  $M$  values.

The trial-and-error procedure described previously (1) was used to match the experimental and theoretical  $I'$  profile of the (002) band. This process leads to a picture of the distribution of  $M$  values characterizing each sample, which is to say, the weight fractions of graphite-like (aromatic) layers combined into crystallites composed of one layer ( $f_1$ ), two layers ( $f_2$ ), three layers ( $f_3$ ), etc. Although this frequently leads to rather precise fitting of the (002) profile, it does not mean that the solution is unique. In fact, a study of the effect of controlled variations of  $f_1$ ,  $f_2$ ,  $f_3$ , etc., upon the quality of the fit obtained has shown that rather large deviations may be tolerated in  $f_1$ ,  $f_2$ , and  $f_3$  provided only that they are mutually complementary ( $f_2$  increased at the expense of  $f_3$  for example). This leads to the following estimate of probable deviations which apply to the various  $f$ 's:

$f_1$	$\pm 0.05$
$f_2, f_3$	$\pm 0.03$
$f_4, f_5, f_6$	$\pm 0.02$
$f_7, \dots, f_{12}$	$\pm 0.01$

These limits should be kept in mind in comparing the  $M$  distributions of the fourteen samples represented by histograms in Figure 2. These include six electrode binder pitches and their cokes and a beta resin and its coke. To emphasize the effect of coking at 575° C. on the association of layers, the coke histogram (broken lines) of each specimen has been superposed upon the histogram of the corresponding uncoked specimen (solid lines). It is evident that coking results in an increased degree of association of layers, the histograms tending to extend to higher  $M$ 's with a decrease in the  $f$ 's at lower  $M$ 's. It is interesting to note, however, that in some cases coking increases the weight fraction of single layers,  $f_1$ , and in other cases decreases it.

Figure 3 compares the  $I'$  (002) profiles of pitch No. 3 and its coke. The greater asymmetry of the pitch profile is typical of all the specimens studied to varying degrees. It is probably the consequence of a considerable variation in the interlayer spacing,  $d_M$ . The nature of the skewness can be explained by crystallites with comparatively few layers having larger values of  $d_M$  than those with more layers. Semi-quantitative efforts to determine the upper and lower limits on  $d_M$  result in maximum values as large as 4.0 Å. if the minimum value of 3.44 Å. proposed by Franklin (7) for disordered layers is accepted. The presence of aliphatic material would also contribute to skewness of the type observed, and this would result in calculated  $d$  values which are too small. However, the aromatic content of the pitches studied is

so high as to eliminate this as a substantial source of error.

It is not possible to achieve a completely satisfactory matching of theoretical and experimental profiles for such skewed profiles on the basis of a single value of  $\underline{d}_M$ , as is done in the present scheme of analysis. At the same time the mathematical complexities arising from the use of a variable  $\underline{d}_M$  parameter are so great as to exclude this approach in practice. It is well to bear in mind, then, that the  $\underline{M}$  distributions deduced for the pitches are somewhat less reliable than those for the cokes, which produce more symmetrical  $\underline{I}'$  (002) profiles.

Table I lists the  $\underline{L}_a$  and  $\underline{L}_c$  dimensions of the crystallites together with the parameters  $\underline{D}$ ,  $\underline{d}_M$ , and  $\underline{M}_e$ , which were described earlier. The effective number of layers per crystallite is defined by

$$\underline{M}_e = \sum_M f_M M, \quad (5)$$

and  $\underline{L}_c$  is then given by

$$\underline{L}_c = \underline{d}_M \underline{M}_e = \underline{d}_M \sum_M f_M M. \quad (6)$$

In equation (6)  $\underline{d}_M$  is computed from the  $\underline{s}$  value corresponding to the point of maximum intensity of the  $\underline{I}'$  (002) profile using the relation

$$\underline{d}_M = 1/s_{\max}. \quad (7)$$

It is to be emphasized that a single but different experimental value of  $\underline{d}_M$  is derived for each specimen, but that a single constant value of 3.52 Å. has been employed in the computation of all the theoretical (002) profiles in order to keep the mathematical labor within bounds.

In Table II values of the "shape factor"  $\underline{L}_a/\underline{L}_c$  have been computed for the six pitches and their cokes as well as for the uncoked and coked beta resin. These ratios make use of  $\underline{L}_a$  from the (11) peak width and  $\underline{L}_c$  as derived from (002) profile matching, which are considered to be the most reliable values. From the two tables it will be seen that the layer dimension  $\underline{L}_a$  falls in the range 12-16 Å. for both the pitches and the cokes, while the crystallite "height"  $\underline{L}_c$  lies in the range 12-14 Å. for the pitches but 16-19 Å. for their cokes. Hence the pitch crystallites have approximately equal dimensions  $\underline{L}_a$  and  $\underline{L}_c$  (average  $\underline{L}_a/\underline{L}_c = 1.07$ ), whereas when coking occurs the crystallites grow more rapidly along  $\underline{c}$  than  $\underline{a}$  (for cokes the average  $\underline{L}_a/\underline{L}_c = 0.77$ ).

From Table I it is seen that so-called "disorganized matter" constitutes from 30 to 50% of the mass of both the pitches and their cokes. This is appreciably higher than in carbon blacks where the usual limits are between 10 and 35%. It is also somewhat surprising that the fraction of disorganized matter in pitches is not appreciably larger than in their cokes. We may again note in this connection that the presence of aliphatics would tend to result in an underestimation of  $\underline{D}$ .

In order to understand what disorganized matter means we must remember that all x-ray interference effects, both crystalline reflections and amorphous halos, are the result of x-ray scattering by pairs of atoms separated by a frequently encountered vector distance or by systems of atoms arranged in a periodic fashion (lattices). On the other hand all interatomic vector distances of random, or very irregular, lengths result in continuous diffuse scatter which is part of the background scatter of the diffraction record. It is this continuous scatter, indistinguishable from the theoretical independent scatter of isolated atoms, which is interpreted by the present analytical method as being due to disorganized material. Therefore, disorganized matter consists only in part of fragmentary aggregates of carbon and other atoms. A

Table I. Crystallite Structure Parameters of Six Electrode Binder Pitches and a Beta Resin and Their 575° C. Cokes

(W-F = Warren-Franklin analysis)

	<u>D</u>	<u>L<sub>a</sub></u> (A.) (W-F)	<u>L<sub>a</sub></u> (A.) (width)	<u>L<sub>c</sub></u> (A.) (distrib.)	<u>L<sub>c</sub></u> (A.) (width)	<u>d<sub>M</sub></u> (A.)	<u>M<sub>e</sub></u>
Estimated Precision (probable deviation)	±0.05	±1.5	±1.5	±0.5	±0.5	±0.03	±0.20
1. Pitch	0.44	16.3	13.2	14.1	14.3	3.51	4.03
Coke	0.42	17.1	12.0	18.8	27.8	3.48	5.41
2. Pitch	0.39	14.5	15.3	12.7	13.9	3.52	3.60
Coke	0.36	14.2	13.1	17.8	26.4	3.52	5.05
3. Pitch	0.48	14.2	13.5	13.5	13.2	3.57	3.79
Coke	0.32	10.8	15.3	15.8	22.5	3.47	4.56
4. Pitch	0.44	15.6	12.1	12.4	12.9	3.52	3.51
Coke	0.51	20.0	12.4	17.3	22.5	3.50	4.95
5. Pitch	0.44	13.4	16.4	11.8	11.8	3.60	3.27
Coke	0.43	18.0	14.1	18.1	24.0	3.47	5.23
6. Pitch	0.46	10.4	12.4	12.6	13.2	3.52	3.59
Coke	0.45	12.0	13.3	16.4	27.5	3.50	4.69
7. Beta resin	0.52	23.8	13.9	12.0	12.5	3.55	3.39
Beta resin coked	0.38	17.6	14.8	19.1	18.0	3.55	5.39

Table II. Shapes of Crystallites  
( $L_a/L_c$  = ratio of diameter to height)

Sample No.		$L_a/L_c$ of Pitches	$L_a/L_c$ of Cokes (575° C.)
1		0.94	0.64
2		1.20	0.74
3		1.00	0.97
4		0.98	0.72
5		1.39	0.78
6		0.98	0.81
	Average	1.07	0.77
7	Beta Resin	1.16	0.78

considerable, if not major, part consists of other atoms irregularly located with respect to their nearer neighbors. Another way of saying this is that all departures of the atomic arrangement in the sample from ideality (ideal graphite layers associated in a random layer lattice), which is to say structural imperfections, will contribute to the diffuse background scatter and be recognized in part as disorganized matter. Thus the following will be interpreted, at least in part, as disorganized matter: foreign atoms (O, N, S, H, etc.), variations in the interlayer spacing from whatever causes, buckling of the layers due to possible non-aromatic character in certain regions, holes in the aromatic layers, and translational irregularity in the stacking of the layers one upon the other. J. R. Townsend (18) has made theoretical studies which show quantitatively that this kind of stacking disorder reduces the intensity of the (002) band and at the same time contributes to the diffuse background.

#### SMALL-ANGLE X-RAY ANALYSIS

Experimental Procedure. The x-ray scattering intensities at small angles were recorded manually using a General Electric XRD-5 diffraction apparatus equipped with a pair of identical  $0.05^\circ$  slit collimators (Type 4954BE) and argon proportional counter tube (Type A4952E). As in the wide-angle measurements, balanced nickel and cobalt filters were used to provide x-ray intensities of relatively high monochromatic character. Figure 4 is a schematic drawing of the apparatus with the receiving collimator (No. 2) set at the  $0^\circ 2\theta$  position so as to receive the direct beam transmitted by collimator No. 1. The specimen is oriented with its surface normal to the direct beam. It turns through an angle  $\Delta\theta$  about the spectrogoniometer axis when the receiving system turns through an angle  $2\Delta\theta$ , as is the usual arrangement in powder diffractometers. Although this causes the specimen to be inclined slightly when the small-angle scattering is being recorded, the x-ray absorption correction is not perceptibly changed because of the small angles involved. This means that an absorption correction need not be included in the interpretation of the intensity data. The slits 1a, 1b, 2a, and 2b are of equal dimensions, the width being about 0.04 mm. and the height being comparatively very large and determined by the separation of the Soller plates. These are sets of parallel plates with a spacing chosen so as to limit the vertical divergence to a tolerable amount.

The specimen powders were packed in a rectangular window 0.2 cm. thick by 0.4 cm. wide by 1.38 cm. long in a brass plate, no binders or adhesives being used. In terms of the specimen weight  $w$ , volume  $v$ , and known solid density  $d_s$ , the volume fraction of solid matter is then

$$c = \frac{\text{macro density}}{\text{solid density}} = \frac{w}{d_s v}$$

The volume fraction of void space is, of course,  $1 - c$ . Counting rates were recorded point by point from  $2\theta = 0.04^\circ$  to a maximum angle beyond which the intensity was too low to measure accurately without prohibitively long counting times. This upper angular limit ranged from  $0.3^\circ$  for some pitches, quinoline soluble fractions, and the beta resin to  $1.0^\circ$  for all of the quinoline insoluble fractions. For each specimen the scattering curve was recorded (a) with Ni filter, (b) with Co filter, and then with specimen removed (c) with Ni filter, and (d) with Co filter. The difference of curves (c) and (d) gives a measure of the correction to be applied for parasitic scattering (scatter due to slits, air, and other extraneous sources). The correction curve is obtained by multiplying the directly measured curve by the absorption factor characterizing the particular specimen being examined,  $\exp(-\mu t)$ , where  $\mu$  is the linear absorption coefficient of the sample and  $t$  is its thickness. The exponent  $\mu t$  can be directly obtained from the weight-to-area ratio ( $w/A$ ) of the specimen by the following transformation:

$$\mu t = \frac{\mu}{d_s} \times \frac{d_s t A}{A} = \frac{\mu}{d_s} \times \frac{w}{A} . \quad (8)$$

In this expression  $(\mu/d_s)$  is the mass absorption coefficient of the specimen for x-rays and  $A$  is the area of the face of the specimen normal to the beam ( $0.4 \times 1.38 = 0.552 \text{ cm.}^2$  for the specimen holder employed). The composition of each of the specimens was regarded as being 100% carbon, for which  $\mu/d_s$  was assigned the value measured by Chipman, (3) 4.15. Hence in the present study  $\mu t = 7.52 w$ . The intensity curve to be analyzed was obtained from the several measured curves as follows:

$$I = (I_{Ni} - I_{Co})_S = (I_{Ni} - I_{Co})_{NS} \exp(-\mu t).$$

Here  $S$  = sample and  $NS$  = no sample.

Interpretative Procedure and Results. For a full explanation of the interpretative procedure the reader is referred to the paper by Kahovec et al. (9) Guinier and Fournet (8) have given a condensed account of the theory and requisite experimental conditions. The necessity for making corrections for finite slit height has been avoided by employing slits of large height-to-width ratio. The theory takes into account this experimental feature implicitly, (9,16) so that the formulas presented herewith require no modification for the "slit effect".

The first step in the analysis of the intensity curves is to compute the following quantities:

$$e = \int_0^{\infty} I ds . \quad (9)$$

$$q = \int_0^{\infty} I s ds . \quad (10)$$

$$a = \lim_{s \rightarrow \infty} (I s^3) . \quad (11)$$

In these expressions  $s = (4\pi \sin \theta)/\lambda$ , or  $4\pi\theta/\lambda$  since  $\theta$  is very small. It is seen that  $e$  is the integral scattered intensity over the entire range of appreciable intensity. Its value cannot be determined accurately in cases where  $I$  is still increasing rapidly at the lowest angle attainable. It can be shown theoretically that the scattering curve must in a completely general way approach asymptotically the line  $s^{-3}$  at higher angles, so that if the curve is multiplied by  $s^3$  a constant limiting value of  $a$  is reached. When this condition is experimentally realized, it becomes possible to determine the specific surface of the specimen. For some types of heterogeneity this asymptotic value is not reached at angles for which  $I$  is of detectable intensity, in which event the specific surface cannot be determined directly. A convenient way to apply this initial criterion is to plot intensity against  $s$  (or  $2\theta$ ) on log-log paper and note whether a slope of approximately -3 is reached at the highest angles. This log-log plot also reveals something of the type of structure of the colloidal system. A flat mid-section means rod- or plate-like particles rather than a spherical or granular habit, a steeper slope as the primary beam is approached indicates clustering of particles into larger aggregates, while a decreasing slope as the primary beam is approached denotes the presence of a considerable proportion of particles of relatively small size. If the slope is uniformly close to -3 throughout the measurable range, the particles are regarded as rather uniform in size and approximately spherical in shape.

If an asymptotic slope of -3 is reached at the higher angles, the total surface area can be computed in terms of the volume fraction of solid from  $a$  and  $q$  as follows:

$$O = 4Vc (1 - c) a/q, \quad (12)$$

from which the surface in  $m.^2$  per  $cm.^3$  of solid sample is

$$O_r = \frac{O}{V_c} = 40,000 (1 - c) \frac{a}{q}, \quad (13)$$

and the specific surface in  $m.^2$  per g. is

$$O_{sp} = \frac{40,000 (1 - c) a}{d_s q}. \quad (14)$$

The theoretical expressions set forth by Porod, Kahovec, and associates also include three other useful quantities. The first is  $f$ , the structure number, defined by

$$f = ea/q^2. \quad (15)$$

This quantity is qualitatively a measure of the irregularity of the colloidal subdivision. In a dilute system of identical spheres  $f$  is about  $1/2$ . Cluster formation, fluctuations in particle size, and deviations from spherical shape cause an increase in  $f$ , so that for granular structures in general it is close to unity. Still larger  $f$ 's indicate pronounced departures from spherical shape.

The theory also yields two length parameters,  $\bar{l}$  and  $l_c$ . The first is the inhomogeneity length,

$$\bar{l} = 40,000/O_r. \quad (16)$$

If the colloidal system is imagined to be pierced by rays in all directions at random, the rays will be cut into different lengths by the disperse phase (particles in void or holes in solid). The numerical average of these lengths is  $\bar{l}$ . The second length parameter,  $l_c$ , is known as the coherence length and is given by

$$l_c = 2e/q. \quad (17)$$

It is related to the size and shape of the particles as well as to their arrangement. In a dilute system of identical spheres  $l_c$  is equal to  $3/4$  of the sphere diameter. Clustering of particles will cause an increase in the value of  $l_c$ .

Table III gives results for three electrode binder pitches and their cokes, quinoline insoluble (Q.I.) fractions, and quinoline soluble (Q.S.) fractions, and for a beta resin. Figure 5 shows the plots of  $\log \bar{l}$  against  $\log 2\theta$ . Before attempting an interpretation of the numerical data in Table III it is best to see what can be learned from the curves. Perhaps the most obvious feature of the curves is their similarity in shape. With few exceptions they slope upwards at the lowest angles, an indication of either particle clustering or the presence of a substantial weight fraction of much larger particles. This is a conspicuous characteristic of all the specimens except the quinoline insoluble fractions, of which only one displays this feature. The slopes of all the curves tend to decrease continuously, although sometimes irregularly, with increasing angle. Hence there is no indication of pronounced departure from a spherical particulate habit. Finally, for most of the specimens the slopes

Table III. Small-Angle Scattering Results for Selected Samples

	Scattering Range ( $^{\circ}2\theta$ )	$\bar{e}$ (arbitrary units)	$\bar{f}$ (value directly computed)	$\bar{f}$ (value used in computing $\bar{e}$ and $\bar{O}_{sp}$ )	$\bar{e}$ (A.)	$\bar{e}$ (A.)	$\bar{O}_{sp}$ (m. <sup>2</sup> /g.)
Pitches							
No. 1	0.04-0.3	247	0.42		542		
No. 3	0.04-0.3	373	0.39		540		
No. 6	0.04-0.3	210	0.45		545		
Cokes							
No. 1	0.04-0.6	749	0.55	0.60	446	619	37.0
No. 3	0.04-0.7	1600	0.43	0.60	437	629	36.3
No. 6	0.04-0.6	1046	0.45	0.60	463	574	40.0
Q.I. Fractions							
No. 1	0.04-1.0	2939	0.38	0.60	423	623	39.0
No. 3	0.04-1.0	3832	0.54	0.54	384	698	34.7
No. 6	0.04-1.0	5333	0.59	0.59	362	577	42.0
Q.S. Fractions							
No. 1	0.04-0.3	446	0.34		548		
No. 3	0.04-0.3	230	0.43		541		
No. 6	0.04-0.4	706	0.42		527		
Beta Resin	0.04-0.3	786	0.49		518		

become considerably less than  $-3$  at the largest angles, which means that in these instances the surface areas will have to be estimated by an indirect approach rather than determined directly in terms of the limiting value of  $a = I_s^3$ . Kahovec et al. suggest for such cases that a reasonable value be assigned to  $f$  and that a value of  $a$  be computed from it by means of equation (15). In Table III this method has been followed for cokes 1, 3, and 6 and Q.I. fraction 1, using an assigned  $f$  value of 0.60. The corresponding  $\underline{I}$  and  $\underline{Q}_{sp}$  values are therefore to be regarded as estimates and less accurate than the values for Q.I. fractions 3 and 6.

The observations just made are in accord with the small values of  $f$  directly computed from the experimental intensities by means of equation (15). For Q.I. fractions 3 and 6 the limiting slope of the  $\log \underline{I}$  versus  $\log s^3$  curve is close to  $-3$ , permitting dependable specific surface values to be calculated using equation (14). For the other samples the slopes become  $-3$  at intermediate angles and yield the directly computed  $f$  values given in Table III, many of which are smaller than the theoretical minimum value of 0.50 to be expected for an ideal system of uniform spheres. These abnormally small values are not unexpected since a slope of  $-3$  at large angles is not reached. A choice of  $f = 0.60$  seems reasonable as a basis for subsequent calculation of  $a$ ,  $\underline{L}$ , and  $\underline{Q}_{sp}$  since this is approximately the value observed for Q.I. fractions 3 and 6, which are believed to be reliable. The fact that all the directly computed  $f$ 's are in the neighborhood of 0.5 emphasizes what has been already inferred from the curves, that the particle shape is not far from spherical.

It will be seen from Table III that the amount of small-angle scattering,  $\underline{e}$ , is largest for the Q.I. fractions, considerably less for the cokes, and very small for the pitches and Q.S. fractions. This shows that the Q.I. samples are most heterogeneous physically, the cokes less so, and the pitches and Q.S. samples relatively homogeneous. The weak small-angle scattering of the last two materials can be interpreted in two ways. First, it may mean that the samples are very largely solid continuums, without pores or particles, but that a small portion of each sample is either particulate or consists of solids with pores. Second, it may mean that the samples are entirely solid without pores or particles, but that the solid continuum consists of regions of differing density. The latter explanation seems more reasonable in the case of pitches and Q.S. fractions, but since the densities of the hypothetical constituent regions are not known, it is not worthwhile to compute specific surface values, which would necessarily rest on extremely arbitrary assumptions. Even if an effective "internal" surface could be computed in this way, it would have only a very ambiguous physical significance. In this connection it may be emphasized that small-angle scattering cannot differentiate between particles in void and the complementary case of pores in solid. Precisely complementary structures of these two kinds would give identical small-angle scattering patterns. Likewise, the specific surface would be the same in both cases and its determination unambiguous.

One of the two length parameters, the coherence length  $\underline{L}_c$ , is computed directly from the intensity integrals  $\underline{e}$  and  $\underline{q}$  (see equation (17)) and can be derived independently of the  $-3$  slope criterion discussed above. Accordingly  $\underline{L}_c$  has been calculated for all the specimens in Table III, whereas  $\underline{L}$ , the inhomogeneity length, and  $\underline{Q}_{sp}$ , the specific surface, have been determined only for the cokes and Q.I. fractions. In deriving the specific surfaces, the values of  $\underline{c}$  used have been those calculated from the following "solid" densities: 1.75 g./cm.<sup>3</sup> for cokes and 1.65 g./cm.<sup>3</sup> for Q.I. fractions.

Not only do the x-ray results indicate an approximately spherical habit for all the materials studied, but the length parameters  $\underline{L}_c$  and  $\underline{L}$  and the specific surfaces are surprisingly similar. This is striking in view of the probable difference in character of the heterogeneity in cokes and in Q.I. fractions. Thus one may be predominantly particulate whereas the other may be more reticular (pores in solid). Electron photomicrographs of the Q.I. fractions confirm the small-angle scattering results by showing most of the particles to be spherical, a considerable portion

being less than 1000 A. in diameter and the rest much larger on the average. Most of the cokes, however, are seen to consist of roughly equidimensional particles of otherwise irregular shape, many of them too large to produce small-angle scattering in the accessible angular range.

In the absence of supplementary information regarding the character of the heterogeneity in a substance that produces small-angle x-ray scatter, it is best to look upon  $L_c$  and  $L$  as giving the approximate linear dimensions of the structural entities responsible for the small-angle scatter instead of attempting a more concrete interpretation in terms of sphere or pore diameters. For all five substances studied these scattering entities are of nearly the same mean size, and in addition they are not far from spherical (at least equidimensional) in shape.

#### CONCLUSIONS

1. The fine structure of electrode binder pitches and their cokes resembles that of carbon blacks. Approximately two-thirds of the carbon is present as aromatic, or graphite-like layers, which for the most part are in turn aggregated into turbostratic crystallites.
2. Roughly one-third of the carbon and minor constituent elements are present as so-called disorganized material, a higher proportion than in carbon blacks.
3. The pitch and coke crystallites are approximately equidimensional with linear dimensions of 12-20 A. Coking of a pitch at 575° C. produces a somewhat greater increase in  $L_c$  than in  $L_a$ .
4. The interlayer spacing in pitch crystallites shows considerable variation, in contrast with those in cokes or carbon black, which are rather uniform.
5. A considerable portion, probably more than half, of the quinoline insoluble fractions examined is present in the form of roughly spherical particles with a mean diameter of the order of 500 A. The remainder is present as much larger particles the dimensions of which cannot be measured by small-angle x-ray scattering.
6. The small-angle scattering produced by pitches and their quinoline soluble fractions is weak, showing that they possess little if any particulate character.
7. 575° C. cokes of pitches and the quinoline insoluble fractions of pitches possess similar specific surfaces of the order of 40 m.<sup>2</sup>/g.

#### ACKNOWLEDGMENTS

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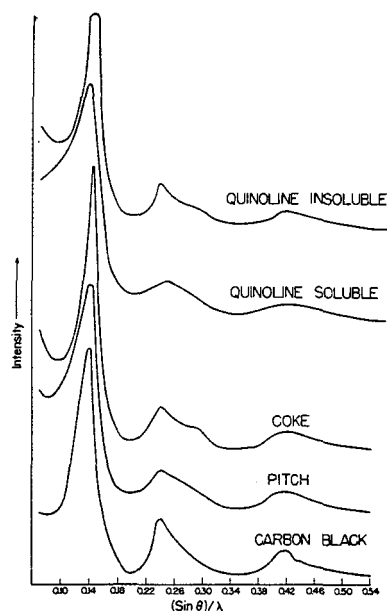


Figure 1. Comparison of the wide-angle x-ray diffraction patterns of an electrode binder pitch, its 575° C. coke, quinoline soluble and insoluble fractions of a pitch, and a typical carbon black

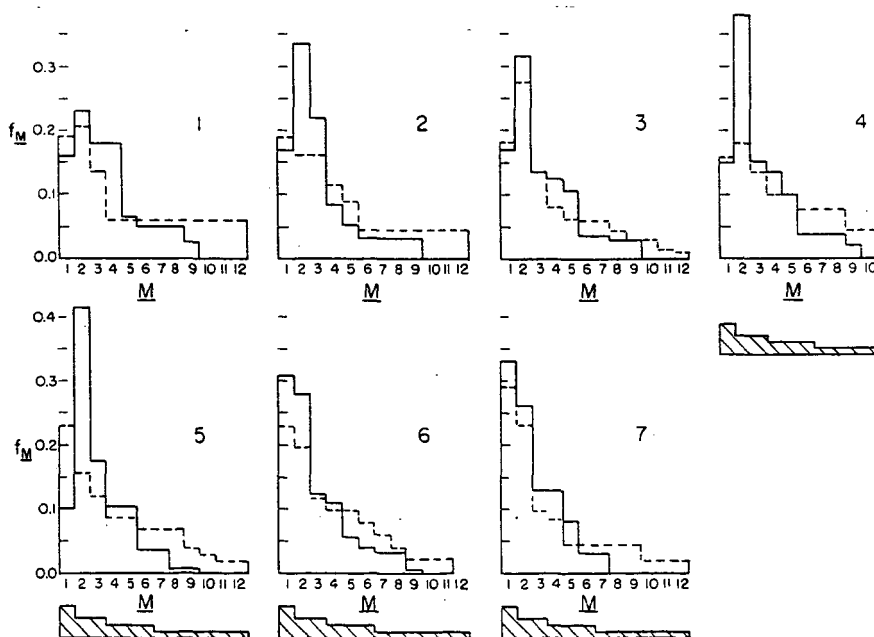


Figure 2. Histograms comparing the  $M$  distributions in six pitches (Nos. 1-6), a beta resin (No. 7), and their respective 575° C. cokes. Solid lines uncoked, broken lines coked. Estimated precision of  $f_M$ 's indicated by hatched histograms.

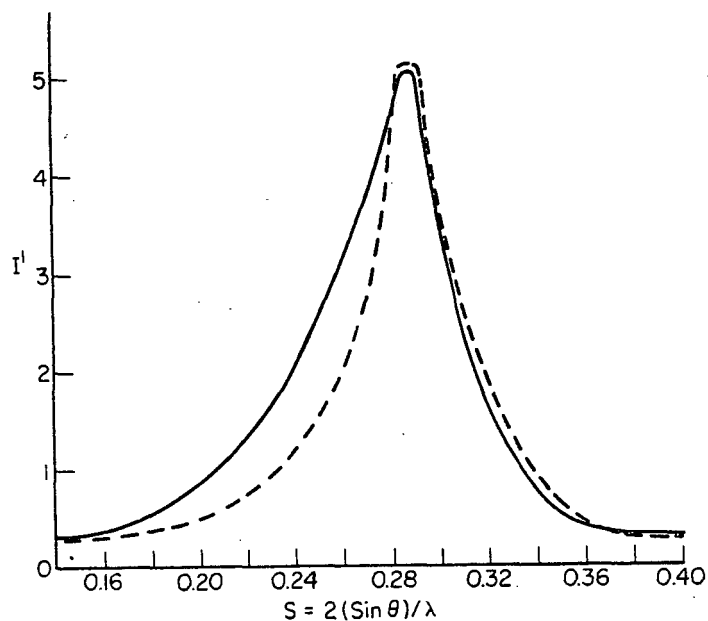


Figure 3. Comparative (002) profiles of pitch No. 3 (solid line) and its 575° C. coke (broken line).

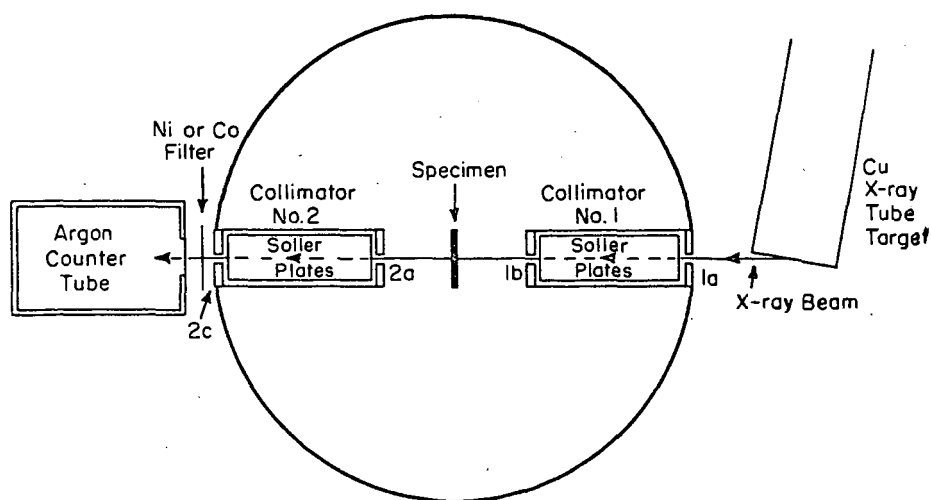


Figure 4. Schematic diagram of small-angle scattering apparatus.

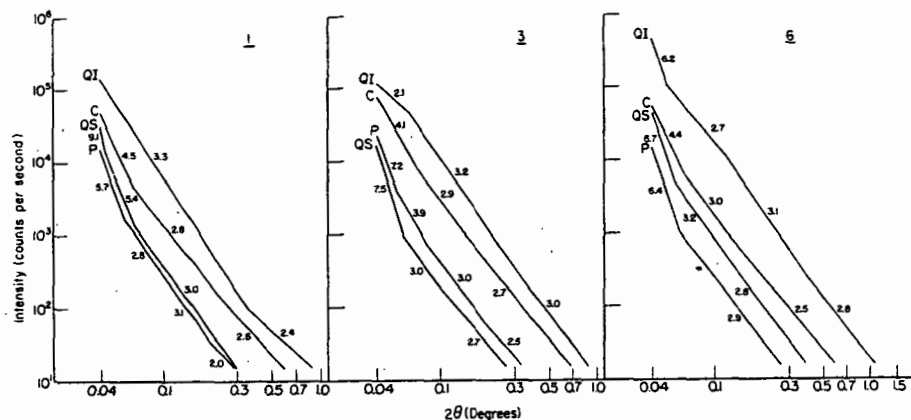


Figure 5. Plots of  $\log_{10} I$  versus  $\log_{10} 2\theta$  for three electrode binder pitches (P), their 575° C. cokes (C), quinoline insoluble fractions (QI), and quinoline soluble fractions (QS). Numbers on curves indicate magnitudes of the negative slopes.

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The Relation of the Chemical and Physical Properties of Coal  
Tar Pitches to their Carbonization and Graphitization Character

P.L. Walker, Jr., C.R. Kinney, D.O. Baumbach, and M.P. Thomas  
Fuel Technology Department, The Pennsylvania State University  
University Park, Pennsylvania

INTRODUCTION

Coal tar pitch, derived from by-product ovens, is the preferred material for use as a binder in the manufacture of carbon and graphite electrodes. Variations in the type of coke oven and coke oven practice and the diversity of sources of supply give rise to variations in pitch quality which affect electrode performance and result, in the case of some pitch binders, in poor performance. At the moment, it seems in vogue for industry to invariably blame poor electrode performance on the binder, despite variations in the properties of the filler (usually petroleum coke), which may be as great as those variations in binder properties. It appears that the main justification for attributing poor electrode performance to the binder is the feeling that coal tar pitch coke does not grow in crystallite size as markedly as does petroleum coke upon heat treatment. With the attendant smaller growth in crystallite size, it is suggested that the pitch binder possesses inferior quality for such important properties as electrical and thermal conductivity, reactivity to gases, coefficient of thermal expansion, and strength.

The three initial aims of this research have been: (1) to seek relationships between the chemical and physical properties of coal tar pitches and the properties of the cokes and graphitized carbons produced therefrom; (2) to better understand the effect of heat treatment temperature on the properties of carbons produced from coal tar pitch; and (3) to compare the properties of the cokes and graphitized carbons produced from coal tar pitch with those produced from a standard, commercially used petroleum coke. For reaction rate studies, comparisons are also made with a coal coke and lampblack. This paper presents the results on this initial phase of research.

Work is now in progress studying the interaction between the filler and binder phases. Selected pitches from those examined in the initial phase of the research are being processed with a standard petroleum coke in a conventional manner to produce carbon and graphite bodies. Important properties of the bodies will be compared with the same properties of the cokes and graphites produced separately from the pitches in an attempt to learn the real significance of binder properties in affecting electrode performance. The results of this latter phase of research will be reviewed at a future date.

## EXPERIMENTAL

### A. Preparation of Coke and Graphitized Carbons

1. Charring of the coal tar pitches. A sample of 250 grams of coal tar pitch was placed in an annealed glass liner (5.4 cm. o.d. and 52.5 cm. long). The liner was enclosed in a gas-tight steel bomb (1780 cc. capacity) and the bomb was evacuated prior to filling with nitrogen to atmospheric pressure. The bomb was heated to  $550 \pm 2.5^\circ\text{C}$ . in twelve hours and held at  $550^\circ\text{C}$ . for an additional twelve hours. The maximum pressure developed on charring ranged from 710 to 890 psig., depending upon the pitch. The bomb was allowed to cool to room temperature before opening.

The recovery of char inside the glass liner, which was subsequently coked and graphitized, generally ranged from 67 to 78 per cent of the initial pitch weight. The remainder of the weight could be accounted for by char between the glass liner and bomb wall and by permanent gases. The molecular weight of the permanent gases was estimated in several runs to be about 22. Two charring runs were made on each pitch, with the charring yields agreeing consistently within 1.5 per cent.

2. Grinding of the coal tar pitch chars. The pitch-chars were ground in a hammer mill and screened through U.S. sieves 40 and 60 mesh. The 40 x 60 mesh fraction, which amounted to between 30 and 40 per cent of the char yield, was used in the subsequent coking operation.

3. Coking of the coal tar pitch chars. Twenty-five grams of char from each charring run were heated (in a Vycor tube flushed with helium) at a rate of  $5^\circ\text{C}$ . per minute to  $1000^\circ\text{C}$ . and soaked for one hour at this temperature. Variation in temperature along the sample length was less than  $\pm 6^\circ\text{C}$ . The coke yield amounted to about 65 to 70 per cent of the initial pitch weight. Negligible fusing of the 40 x 60 mesh char particles was found on coking.

4. Graphitization of the coal tar pitch cokes. Approximately 10 grams of 40 x 60 mesh coke were placed in cylindrical graphite capsules (1 1/2 in. o.d. and 1 1/2 in. long). The capsules were loaded into a larger cylindrical graphite capsule (4 in. o.d. by 11 in. long), which was then centered in a resistance furnace. The resistance furnace, which was flushed with helium during a run, consisted of a graphite tube 6 inches in diameter and several feet long. Samples were allowed to cool to room temperature before being removed. All temperatures were measured with a Pyro optical pyrometer. Samples graphitized by resistance heating are designated as carbons (R).

5. Additional heat treatment of a variety of carbons. In order to understand the effects of a wide heat treatment range on the subsequent reactivity of coal tar pitch coke, petroleum coke, coal coke, and lampblack to oxidizing gases, samples were heated to temperatures of approximately 1750, 2000, 2250, 2600, and  $2800^\circ\text{C}$ . in an induction furnace, with zero soak time at the maximum temperature. Three cylindrical graphite crucibles (7/8 in. o.d. and 1 1/2 in. long) were partially filled with 5 grams of sample. The crucibles were inserted into a graphite tube (1 1/4 in. o.d. and 21 in. long), which in turn was centered into a quartz tube (3 1/4 in. o.d. and 25 1/4 in. long). The furnace was evacuated over night at room temperature and then flushed with helium during the run. The temperature was regulated by manual control of a transformer. Temperature readings were taken with an optical pyrometer sighted through a quartz window at the top of the furnace.

B. Apparatus and Procedures Used to Define the Properties of the Pitches, Cokes, and Graphitized Carbons

Standard procedures previously described were used in the x-ray diffraction (2), surface area (3,4), electrical resistivity (5), and gas reactivity studies (6). Analyses of the coal tar pitches were determined using standard specification studies (7).

C. Description of Raw Materials

The coal tar pitches represent the residual product from the distillation of high-temperature coke-oven tars. No information is available on the carbonization temperatures at which the tars were produced or the distillation procedures used to produce the coal tar pitches.

Raw petroleum coke is the coked still bottoms left in the pot after distillation of the crude oil. The raw coke having seen a temperature of ca. 500°C. was calcined at ca. 1250°C. It had an ash content of 0.12 per cent and a carbon content of 97.8 per cent.

Lampblack is prepared from the partial combustion of liquid hydrocarbons. The lampblack used in this research was taken from crushed, 5/8-in. gas baked (ca. 1000°C.) lampblack electrodes. The green electrodes contained a mixture of 75 per cent lampblack and 25 per cent coal tar pitch by weight. The baked material had an ash content of 0.22 per cent and a carbon content of 98.9 per cent.

The coal coke was a standard low temperature foundry coke produced at about 600°C. It had an ash content of 6.8 per cent and a carbon content of 85.0 per cent.

## RESULTS AND DISCUSSION

A. Analyses of the Coal Tar Pitches

Table I presents data on the chemical analyses of the whole pitches. The analysis for sample BD-PSU-5 is markedly different from the remaining samples, since it is a lignite pitch.

Table II presents semi-quantitative data on the concentration of metallic impurities in some selected pitches. The concentrations were determined using standard spectrochemical techniques. The concentrations are expressed in parts of impurity per million parts of pitch on a weight basis.

Table III presents miscellaneous data on the pitches. The coking values were determined using the Barrett Method B-8 (7), which consists of rapidly heating the pitch to 900°C. and holding the temperature for seven minutes. The softening point of the pitches was determined by the ring and ball method (7). From Table III, it is seen that the specific gravity of the whole pitch increases with an increase in its quinoline insoluble content. Also as expected, it is seen from Table III that as the specific gravity increases, the coking value also increases.

B. Chemical Analyses of the Cokes from the Group A Coal Tar Pitches

Table IV presents data on the chemical analyses of the cokes from the Group A\* coal tar pitches. For these pitches, two charring runs and three coking runs were made, with the char from one run being coked twice. The data, consequently, represent an average of three coking runs. The amount of hydrogen in the original pitch removed upon coking varies from 81 per cent for sample 22805 to 90 per cent for sample 23217. The amount of nitrogen removed from the pitch ranges from 28 per cent for sample 23217 to 100 per cent for sample 56-273. The amount of sulfur removed from the pitch ranges from 28 per cent for sample 22761 to 54 per cent for sample 56-274. Thus, there is considerable variation in the amount of hydrogen, nitrogen, and sulfur removed on coking of the different pitches. However, there is no obvious correlation between the amount of these elements in the original pitch and the percentage of them removed on coking.

C. Crystallographic Parameters for the Chars, Cokes, and Graphitized Carbons from the Group A Coal Tar Pitches

1. Interlayer spacings and crystallite heights. Table V presents data on the interlayer spacings and crystallite heights of the chars, cokes, and graphitized carbons produced from the Group A coal tar pitches. X-Ray diffraction determinations were made on a sample from each run. Consequently, the data on the chars represent the average of two determinations; on the cokes, an average of three determinations; and on the graphitized carbons, an average of two determinations at each temperature (that is, two different samples of coke were heated in each graphitization run). The graphitization runs were performed in the resistance furnace previously described. The interlayer spacing data in all cases are significant to  $\pm 0.02\text{\AA}$ .,  $\pm 0.01\text{\AA}$ ., and  $\pm 0.001\text{\AA}$ . for the chars, cokes, and graphitized carbons, respectively. The crystallite height data in all cases are significant to  $\pm 1\text{\AA}$ .,  $\pm 1\text{\AA}$ ., and  $\pm 50\text{\AA}$ ., respectively.

Franklin (8) and Bacon (9) have thoroughly discussed the use of interlayer spacing data as a criterion of three-dimensional ordering in carbon. Interlayer spacings above  $3.44\text{\AA}$ . are indicative of only two dimensional ordering, whereas decreasing spacings between  $3.44\text{\AA}$ . and  $3.3538\text{\AA}$ . indicate a progressive increase in three-dimensional ordering between zero and 100 per cent. As expected, the interlayer spacing data on the chars and cokes indicate no three-dimensional ordering. Furthermore, for each group the spacings are essentially the same. In line with the findings of Kinney, Nunn, and Walker (10), among others, the interlayer spacings of the material having seen  $1000^{\circ}\text{C}$ . (cokes) are somewhat larger than the comparable material having seen only  $550^{\circ}\text{C}$ . (chars). As expected, the calcined petroleum coke having seen a temperature of ca.  $1250^{\circ}\text{C}$ . has a lower interlayer spacing than the cokes from the coal tar pitches. That is, the interlayer spacing of carbons begins to decrease markedly at heat treatment temperatures above about  $1050^{\circ}\text{C}$ .

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\* The first six coal tar pitches, on which some additional work was done, will be called Group A pitches hereafter. The remainder of the pitches will be called Group B.

On graphitization, a marked decrease in interlayer spacing of all the cokes is seen. The effect of increasing graphitization temperature on further decreasing the interlayer spacing is also evident, as previously discussed (11). The carbon produced from pitch 23217 by graphitization at 2650°C. is seen to have the lowest interlayer spacing, 3.359A., and, consequently, the highest degree of three-dimensional ordering, ca. 85 per cent. The petroleum coke graphitized at 2570°C. has a lower interlayer spacing than the majority of the pitch cokes graphitized at the same temperature. Unfortunately, the petroleum coke was not heat treated at 2650°C.

From Table V, it is seen that there is little significant difference in the average crystallite heights between the chars, as a group or between the cokes, as a group. Some decrease in the average crystallite sizes of the cokes over the comparable chars are noted, in line with previous findings (10). The petroleum coke has a considerably higher crystallite height than any of the pitch cokes, as expected because of its higher calcination temperature. Extensive increases in average crystallite heights of the pitch cokes on graphitization are noted. However, the effect of increasing the graphitization temperature from 2570 to 2650°C. on increasing the crystallite heights is not indicated clearly by the data. In any event, the marked decrease in interlayer spacing and increase in crystallite height upon heating to graphitization temperatures clearly stamp these pitch cokes as "graphitizable carbons".

2. Orientation of crystallites in pitch cokes. As pointed out, the interlayer spacing and crystallite height data on the pitch cokes show such minor variations that it is difficult to distinguish between the samples. A similar situation was shown to exist when a series of calcined petroleum cokes was examined by x-ray diffraction (12). However, in the latter case it was shown that the extent of crystallite orientation in the cokes, as given by the intensity of the (002) x-ray diffraction peak, varied considerably and could be used to predict important properties of carbon bodies made from the cokes. Consequently, relative intensities of the (002) peak for the pitch cokes were determined using techniques previously described (2,12). Peak intensities were determined on the three coke samples from each pitch, and one additional intensity determined on a second sample of one of the cokes selected at random. The average peak intensity for the cokes from each pitch varied in all cases by less than  $\pm 10$  per cent. The intensities varied from 24.4 c.p.s. for pitch coke 22761 (poorest crystallite orientation) to 34.4 c.p.s. for pitch coke 23217 (best crystallite orientation).

D. Surface Areas of the Chars, Cokes, and Graphitized Carbons from the Group A Coal Tar Pitches

Table VI presents surface area data on 40 x 60 mesh samples of coke and graphitized carbons produced from the Group A coal tar pitches. The surface area for the char produced from pitch 23217 is also included. Determinations were made on the same number of samples as in the x-ray diffraction studies, with the average surface areas reported in Table VI representing all samples from a given pitch within at least  $\pm 10$  per cent.

The first major conclusion to be drawn from the data in Table VI is that the surface areas of the cokes (and char) are quite small. These small areas indicate that the cokes (and char) contain a negligible amount

of open porosity in fine pores. A small area is desirable for a graphitizable carbon since it means that there will be a minimum of discontinuities within the particle to stop crystallite growth. It should be noted that the petroleum coke has a somewhat higher area than the coal tar pitch cokes. This could be due entirely, or in part, to the higher heat treatment temperature of the petroleum coke, since it has been shown that surface areas of some carbons do increase slightly when heated in the range 950 to 1100°C.

No relationship is found between the surface area of the cokes and their graphitizability. For example, carbon from pitch 23217 has the lowest interlayer spacing on heat treatment to 2650°C. but yet does not have the lowest surface area, as seen in Table VI. This lack of correlation is not surprising if the very low values of the surface areas are kept in mind. At 2650°C., the extent of crystallite growth is probably not yet limited by the infrequent pores in the coke particle (11).

From Table VI, it is seen that there is a decrease in the specific surface areas of the cokes on heat treatment to 2570 and 2650°C. At 2650°C., this decrease ranges from 50 per cent for sample 22761 to 13 per cent for sample 22763. The percentage decrease in surface area is seen to be roughly related to the surface area of the coke - the higher its area the greater the percentage decrease. This results in the surface areas of all the graphitized carbons varying much less than the surface areas of the cokes.

Despite the over-all decrease in areas on graphitization, there is some indication that the specific surface area of the graphitized carbons increase slightly in going from 2570 to 2650°C. Perhaps volatilization of some impurities in this temperature range produced slight porosity. It is noted that the surface area of the petroleum coke after graphitization at 2570°C. is ca. 25 per cent greater than the surface area of the graphitized pitch cokes.

Looking at the chemical analyses of the coal tar pitches in Table I, no correlation is found between the percentage of hydrogen, nitrogen, or sulfur in the pitch and the surface areas of the cokes or graphitized carbons produced therefrom.

#### E. Electrical Resistivities of Cokes and Graphitized Carbons

Table VII presents electrical resistivity data on the cokes and graphitized carbons produced from both the Group A and B coal tar pitches. The resistivities of the cokes are seen to be quite similar. Disregarding samples 22761 and BD-PSU-5 (lignite pitch), the resistivities of the remaining pitch cokes vary by only  $\pm 12$  per cent. No correlation is found between the electrical resistivities of the Group A cokes and their crystallographic parameters or surface areas. Presumably, likewise no correlations would exist for the Group B pitch cokes. As expected because of its higher calcination temperature, the petroleum coke has a lower electrical resistivity than any of the pitch cokes.

On graphitization, there is a marked decrease in the electrical resistivities of all samples. Further, as expected (13), the higher

temperature graphitization run\* produced, for each sample, the lower electrical resistivity. As for the cokes, no correlation exists between the electrical resistivities of the graphitized carbons from the Group A pitches and the crystallographic parameters or surface areas of the carbons.

The electrical resistivities for the graphitized petroleum coke are comparable with those for many of the graphitized pitch cokes heated to the same temperature. Actually, the electrical resistivities of the graphitized pitch cokes from samples 23217, 56-274, BD-PSU-8, -12, -16, and -17 are lower than the resistivities of the graphitized petroleum coke.

#### F. Gas Reactivities of Cokes and Graphitized Carbons

1. Reactivities of cokes and graphitized carbons to carbon dioxide at 1150°C. Tables VIII and IX present data for the reactivity of cokes and graphitized carbons from the Group A and Group B pitches, respectively. Clearly, for the majority of the pitch samples, the reactivity of the carbons graphitized between 2570 and 2660°C. is greater than the reactivity of the cokes. Samples 56-274 (graphitized at 2570°C.) and BD-PSU-2 are exceptions. For the Group A coal tar pitches, an increase in graphitization temperature from 2570 to 2650°C. results in a marked increase in reactivity of the carbons to carbon dioxide. To the contrary, for the Group B coal tar pitches (and pitch 22805 from Group A) an increase in graphitization temperature from 2660 to 2680°C. produces a decrease in reactivity, with two exceptions. These exceptions are samples BD-PSU-1 and -18.

It is noted that the wide variation in reactivities of the pitch cokes to carbon dioxide is not carried over to the graphitized samples. For example, considering the Group B pitches, the cokes show a spread in reactivity from 3.5 to 30.8 per cent burn-off in two hours. On the other hand, exclusive of BD-PSU-5 (lignite pitch), the samples graphitized at 2660°C. show a spread in reactivity from only 19.8 to 28.1 per cent.

A qualitative correlation is found between the per cent ash in the coal tar pitches (Table I) and the reactivity of the cokes produced therefrom (Table VIII and IX). Even though there is considerable scatter in the data, in general, higher ash content in the pitch means higher reactivity of the coke towards carbon dioxide. The scatter in the data is to be expected since individual constituents of the impurity phase will have different effects on increasing (or decreasing) the reactivity of the coke. No correlation is found, however, between the concentrations of any individual constituent of the impurity phase in the pitch and reactivity of the cokes.

For the Group A coal tar pitches, the reactivity data of the cokes (as a group) or graphitized carbons (as a group) cannot be explained on the basis of the surface area or crystallographic parameters of these materials.

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\* It is noted that the majority of the Group A samples were graphitized at temperatures lower than those used for the Group B samples. Unfortunately, insufficient samples of the Group A cokes were available to make heat treatment runs at 2660 and 2680°C.

In marked contrast to the increase in reactivity upon graphitization for the majority of the pitch samples, the petroleum coke is seen to undergo a major decrease in reactivity upon graphitization to 2570°C. Further, the reactivity of the petroleum coke is many-fold greater than the reactivity of the majority of the pitch cokes; whereas the reactivity of the graphitized petroleum coke is comparable to that of many of the graphitized pitch cokes!

2. Reactivities of different carbons to carbon dioxide and air as a function of heat treatment temperature. Samples of pitch coke 56-273, petroleum coke, lampblack, and coal coke were heat treated in a helium atmosphere at a series of temperatures, using an induction furnace. Separate runs also were made at selected temperatures on pitch coke 56-273 and petroleum coke in an induction furnace, using a 1 per cent chlorine-99 per cent helium atmosphere. Because of space limitations in the induction furnace, only sufficient sample could be heat treated to enable the making of one reactivity run, each, in carbon dioxide and air. Table X summarizes the data.

In agreement with previous findings where the resistance furnace was used to heat treat the samples, the reactivity of the pitch coke is seen to increase upon being treated to higher temperatures. A maximum in reactivity is found for heat treatment to ca. 2000°C. Another maximum (displaced to a higher temperature than found previously for sample 22805) probably occurs at a temperature above 2800°C. Also as found before, the reactivity of petroleum coke to carbon dioxide shows a marked decrease upon heat treatment. The initial decrease is found to occur between the calcination temperature and a heat treatment temperature of 1750°C. A slight increase in reactivity is suggested with an increase in heat treatment temperature between 1750 and 2250°C. This is followed by a second, sharp decrease in reactivity on heat treatment to 2600°C. No further maximum in reactivity is found for the petroleum coke between 2600 and 2800°C., probably because the gap in heat treatment temperature was too large to uncover a maximum.

Limited data indicate that the success attained in decreasing carbon reactivity by heat treatment in a partial chlorine atmosphere depends upon the carbon and heat treatment temperature. For example, for the pitch coke 56-273, it is seen that the use of a partial chlorine atmosphere during heat treatment at ca. 1750 and 2000°C. markedly decreases the subsequent reactivity of the carbon to carbon dioxide. On the other hand, the use of chlorine at ca. 2250°C. shows little effect. The use of a partial chlorine atmosphere during the heat treatment of petroleum coke at ca. 2000 and 2250°C. also shows little effect on the subsequent reactivity.

It is seen from Table X that heat treatment of lampblack and coal coke over a range of temperatures has a negligible effect on the subsequent reactivity of these materials to carbon dioxide. This is particularly surprising in the case of the coal coke, which undoubtedly underwent a major decrease in ash content on heat treatment at 2600°C.

The effect of heat treatment on the reactivity of pitch coke and petroleum coke to air is seen to be considerably different from the effect of heat treatment on their reactivity to carbon dioxide. The reactivity of

both these materials to air is seen to decrease progressively with increasing heat treatment temperature. Furthermore, the reactivities of the two materials to air for heat treatment temperatures up to 2250°C. parallel each other closely. The use of a partial chlorine atmosphere is seen to decrease markedly the subsequent reactivity of the pitch coke to air at all heat treatment temperatures investigated.

As in the carbon-carbon dioxide reaction, variation in heat treatment temperature is seen to have a negligible effect on the reactivities of lampblack and coal coke to air.

It is readily apparent that the reactivity of carbons to carbon dioxide is much more sensitive to carbon-type than is the reactivity of carbons to air. In the latter case, it is seen that the reactivities of different carbons, following particular heat treatment temperatures, are quite similar.

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TABLE I  
CHEMICAL ANALYSES OF THE FITCHES

Pitch	%C	%H	%N	%S	%Other*	%Ash	Atomic C-H Ratio
22761	93.32	4.20	0.75	0.75	0.98	0.10	1.86
22763	93.43	4.24	0.68	0.52	1.13	0.09	1.85
22805	92.43	4.31	0.88	0.41	1.97	0.24	1.80
23217	92.05	4.52	0.50	0.54	2.39	0.13	1.71
56-273	93.39	4.31	0.92	0.60	0.78	0.08	1.82
56-274	92.95	4.49	0.86	0.35	1.35	0.15	1.74
BD-PSU-1	93.35	4.32	1.08	0.27	0.98	0.17	1.81
-2	91.70	4.55	1.31	0.53	1.91	0.63	1.69
-3	92.77	4.32	1.21	0.58	1.12	0.07	1.80
-4	93.34	4.10	1.10	0.49	0.97	0.05	1.91
-5	81.67	7.31	1.16	0.77	9.09	2.55	0.94
-6	93.34	4.38	1.01	0.30	0.97	0.12	1.79
-7	93.36	4.44	1.00	0.31	0.89	0.14	1.77
-8	93.26	4.40	1.01	0.24	1.09	0.11	1.78
-9	93.18	4.46	1.00	0.32	1.04	0.10	1.76
-10	93.47	4.44	0.98	0.25	0.86	0.05	1.77
-11	93.25	4.49	0.99	0.31	0.96	0.05	1.74
-12	93.31	4.46	1.01	0.31	0.91	0.04	1.76
-13	93.17	4.57	1.00	0.30	0.96	0.03	1.71
-14	93.00	4.20	1.06	0.41	1.33	0.25	1.86
-15	93.08	4.29	1.06	0.47	1.10	0.22	1.82
-16	92.24	4.53	1.11	0.39	1.03	0.06	1.72
-17	92.78	4.65	1.10	0.37	1.10	0.06	1.68
-18	93.13	4.42	1.08	0.37	1.00	0.08	1.77
-19	93.13	4.49	1.11	0.37	0.90	0.08	1.74

\* Includes % Ash

TABLE II

CONCENTRATION OF METALLIC IMPURITIES IN SELECTED PITCHES

CONCENTRATION, PPM

Pitch	Al	B	Ca	Cu	Fe	Mg	Mn	Na	Ni	Pb	Si	Ti
22761	7.4	-	8.4	2.0	128.	2.2	2.8	98.	-	23.	41.	-
22763	6.9	-	3.5	4.5	44.	2.2	1.6	40.	-	22.	17.	-
22805	72.	-	99.	19.	98.	9.6	4.3	206.	-	53	96.	-
23217	22.	-	9.6	1.8	46.	5.2	2.3	220.	-	23.	43.	-
56-273	17.	-	25.	1.3	35.	4.2	2.5	31.	-	19.	72.	-
56-274	36.	-	22.	7.3	116.	12.	9.3	78.	-	69.	48.	-
BD-PSU-2	310.	0.88	110.	5.0	360.	23.	11.	-	21.	11.	510.	25.
-4	12.	0.14	6.4	1.3	58.	2.0	1.2	-	2.8	8.5	120.	1.4
-5	2400.	67.	160.	15.	1200.	180.	160.	-	33.	72.	3100.	260.
-6	100.	0.14	46.	1.6	96.	6.4	7.4	46.	4.5	34.	130.	7.4
-9	97.	0.085	23.	0.92	79.	6.7	4.4	28.	3.0	58.	120.	9.4
-11	28.	0.019	13.	0.63	43.	1.6	1.7	37.	1.8	26.	27.	2.3
-12	27.	0.020	17.	0.90	40.	2.8	4.6	42.	3.5	35.	60.	6.0
-13	59.	0.031	52.	1.1	90.	3.9	9.8	90.	6.1	59.	57.	6.2
-14	170.	0.12	75.	2.9	180.	16.	13.	57.	4.2	68.	360.	16.
-16	24.	0.0062	23.	0.48	86.	3.4	5.8	39.	1.8	56.	22.	1.0
-18	28.	0.016	13.	0.62	98.	3.4	5.2	32.	2.0	41.	43.	1.9
-19	62.	0.028	120.	0.80	150.	7.0	8.5	50.	2.9	60.	100.	4.3

TABLE III  
MISCELLANEOUS PROPERTIES OF THE PITCHES

Pitch	Coking Value	Sp. Gr., 25°C.	Soft. Pt., °C.	% Insoluble in	
				Quinoline	Benzene
22761	44.5	1.328	95.5	14.9	32.1
22763	43.8	1.333	98.0	16.5	36.4
22805	41.0	1.315	95.0	12.8	27.1
23217	44.2	1.292	96.0	7.8	25.2
56-273	43.0	1.320	95.0	13.9	33.2
56-274	39.2	1.305	99.9	12.5	32.0
BD-PSU-1	42.8	1.318	94.6	15.8	32.5
-2	35.7	1.298	100.0	5.7	25.5
-3	40.0	1.318	96.0	13.3	27.1
-4	41.7	1.340	101.8	13.4	27.8
-5	24.8	1.174	103.0	8.6	18.9
-6	41.5	1.313	95.2	13.0	29.4
-7	39.8	1.306	88.7	12.2	28.4
-8	37.5	1.307	94.5	10.2	22.5
-9	36.2	1.300	89.5	9.9	20.2
-10	40.5	1.308	94.7	11.6	28.3
-11	37.1	1.297	87.0	8.8	23.7
-12	36.1	1.299	95.0	7.6	19.6
-13	33.3	1.292	88.5	6.0	17.9
-14	42.3	1.328	96.5	18.1	28.6
-15	40.2	1.314	88.2	17.2	27.2
-16	34.7	1.294	97.0	5.2	17.5
-17	32.3	1.286	85.5	5.1	16.3
-18	40.1	1.306	99.0	10.4	26.9
-19	36.1	1.296	87.5	8.3	24.2

TABLE IV  
CHEMICAL ANALYSES OF THE COKES FROM THE  
GROUP A COAL TAR PITCHES

<u>Coke</u>	<u>%C</u>	<u>%H</u>	<u>%N</u>	<u>%S</u>	<u>% Other</u>	<u>Atomic C-H Ratio</u>
22761	98.16	0.48	0.23	0.54	0.57	17.2
22763	97.68	0.61	0.03	0.35	0.35	13.4
22805	96.53	0.79	0.16	0.26	0.26	10.6
23217	97.96	0.44	0.36	0.26	0.26	18.5
56-273	98.35	0.56	0.00	0.29	0.29	14.1
56-274	98.11	0.75	0.05	0.16	0.16	11.4

TABLE VI  
SURFACE AREAS OF THE CHARs, COKES, AND GRAPHITIZED CARBONS  
PRODUCED FROM THE GROUP A COAL TAR PTICHES

<u>Pitch</u>	<u>Surface Area, m<sup>2</sup>/g</u>			
	<u>Char</u>	<u>Coke</u>	<u>Graphitized Carbon</u>	
			<u>2570°C.</u>	<u>2650°C.</u>
22761	-	0.36	0.18	0.18
22763	-	0.24	0.17	0.21
22805	-	0.26	0.17	0.20
23217	0.38	0.34	0.23	0.21
56-273	-	0.31	0.19	0.20
56-274	-	0.45	0.24	0.28
petroleum coke	-	0.59	0.34	-

TABLE V

INTERLAYER SPACINGS AND CRYSTALLITE HEIGHTS OF THE CHARS, COKES,  
AND GRAPHITIZED CARBONS PRODUCED FROM THE GROUP A COAL TAR PITCHES

Pitch	Interlayer Spacing, A.		Crystallite Height, A.	
	Char	Coke <u>Graphitized Carbon 2570°C. 2650°C.</u>	Char	Coke <u>Graphitized Carbon 2570°C. 2650°C.</u>
22761	3.54	3.58 3.370 3.363	18	14 618 613
22763	3.56	3.57 3.367 3.362	16	15 686 710
22805	3.55	3.57 3.369 3.364	17	14 653 702
23217	3.52	3.55 3.365 3.359	19	15 734 895
56-273	3.53	3.56 3.367 3.363	17	15 (789) 720
56-274	3.53	3.56 3.365 3.362	19	14 738 904
petroleum coke	-	3.51 3.364 -	-	25 -

TABLE VII  
ELECTRICAL RESISTIVITIES AT 2500 PSI. AND 25°C.  
FOR COKES AND GRAPHITIZED CARBONS

Sample	Electrical Resistivity, ohm-cm.		
	Coke	Graphitized Carbon	
		2660°C.	2680°C.
22761	0.050	0.0081 <sup>a</sup>	-
22763	0.038	0.0049 <sup>a</sup>	-
22805	0.040	0.0042	0.0032
23217	0.038	0.0029 <sup>b</sup>	-
56-273	0.038	0.0044 <sup>a</sup>	-
56-274	0.032	0.0029 <sup>b</sup>	-
BD-PSU-1	0.037	0.0032	0.0031
-2	0.035	0.0035	0.0034
-3	0.041	0.0046	0.0038
-4	0.038	0.0042	0.0032
-5	0.049	0.0050	0.0042
-6	0.036	0.0032	0.0030
-7	0.040	0.0030	0.0029
-8	0.038	0.0028	0.0025
-9	0.039	0.0037	0.0029
-10	0.037	0.0036	0.0027
-11	0.035	0.0031	0.0024
-12	0.037	0.0027	0.0026
-13	0.037	0.0034	0.0027
-14	0.040	0.0038	0.0031
-15	0.041	0.0039	0.0030
-16	0.034	0.0026	0.0023
-17	0.034	0.0020	0.0021
-18	0.032	0.0033	0.0023
-19	0.036	0.0035	0.0029
petroleum coke	0.024	0.0031	0.0025

<sup>a</sup> Graphitized at 2570°C.

<sup>b</sup> Graphitized at 2650°C.

TABLE VIII  
REACTIVITIES OF COKES AND GRAPHITIZED CARBONS FROM  
GROUP A PITCHES TO CARBON DIOXIDE AT 1150°C.

<u>Sample</u>	<u>Weight Per Cent Coke</u>	<u>Burn-Off in Two Hours</u> <u>Graphitized Carbon</u>	
		<u>2570°C.</u>	<u>2650°C.</u>
22761	8.7 <sup>a</sup>	16.2 <sup>b</sup>	29.3
22763	9.8	12.4	24.4
22805	8.8	15.0	26.2
23217	7.4	17.6	24.3
56-273	7.6	12.4	31.1
56-274	22.0	15.9	27.0
petroleum coke	55.2	10.7	-

<sup>a</sup> Reactivities on pitch cokes represent average of reactivities determined on individual samples from three different coking runs.

<sup>b</sup> Reactivities on carbons at each graphitization temperature represent average of reactivities on two graphitized coke samples.

TABLE IX

REACTIVITIES OF COKES AND GRAPHITIZED CARBONS FROM  
THE GROUP B PITCHES TO CARBON DIOXIDE AT 1150°C.

<u>Sample</u>	<u>Weight Per Cent Burn-Off in Two Hours</u>		
	<u>Coke</u>	<u>Graphitized Carbon</u>	
		<u>2660°C.</u>	<u>2680°C.</u>
BD-PSU-1	17.7 <sup>a</sup>	24.5 <sup>b</sup>	26.8
-2	30.8	21.1	20.5
-3	8.7	23.0	19.1
-4	5.0	22.9	12.3
-5	30.2	40.3	37.9
-6	16.8	20.1	14.4
-7	15.0	20.5	14.7
-8	11.3	24.3	16.8
-9	14.0	25.0	21.9
-10	8.1	19.8	14.2
-11	8.7	23.8	17.3
-12	6.6	23.6	15.1
-13	3.5	21.7	14.5
-14	16.7	28.1	17.2
-15	17.5	25.7	17.9
-16	14.4	25.1	15.2
-17	11.6	20.8	15.2
-18	12.4	20.0	25.5
-19	14.1	22.7	16.8
22805	8.8	26.8	17.2
petroleum coke	55.2	22.5	15.2

<sup>a</sup> Reactivities on pitch cokes represent average of reactivities determined on individual samples from two different coking runs.

<sup>b</sup> Represents one reactivity run on one graphitized coke sample at each temperature in every case.

TABLE X  
REACTIVITIES OF CARBONS TO CARBON DIOXIDE AND AIR

Sample	Heat Treatment Temperature, °C.	Weight Per Cent Burn-Off in Two Hours	
		Carbon Dioxide at 1150°C.	Air at 700°C.
Pitch 56-273	1000	7.6	25.8
"	1745	27.0	22.8
"	1750 <sup>a</sup>	18.5	20.4
"	2000	28.3	21.3
"	2005 <sup>a</sup>	12.3	12.4
"	2240	11.9	16.1
"	2250 <sup>a</sup>	10.9	10.4
"	2600	6.4	10.4
"	2800	24.5	8.2
Petroleum Coke	1250	55.2	24.8
"	1750	34.4	22.5
"	2020	34.9	20.6
"	2005 <sup>a</sup>	34.6	-
"	2250	37.0	16.2
"	2265 <sup>a</sup>	34.6	-
"	2600	10.6	-
"	2825	11.0	14.4
Lampblack	1000	56.1	26.4
"	2270	57.7	25.5
"	2600	52.3	28.3
Coal Coke	600	49.2	26.5
"	2250	60.5	24.4
"	2600	55.6	25.8

<sup>a</sup> Atmosphere in furnace 1% Cl<sub>2</sub>-99% He